J. L. S. Wales

The application of flow birefringence
to rheological studies of polymer melts

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Summary

This work is concerned with the streaming birefringence of polymer melts. Particular consideration has been made of properties in steady shearing flow. The investigation consists of an experimental and a theoretical part. In the experimental part, the construction of new apparatuses for the measurement of streaming double refraction is described. None of the apparatuses is otherwise commercially available.

1. A cone-and-plate apparatus for the measurement as a function of shear rate of the birefringence and the extinction angle in the 1-2 plane.

This apparatus supplies data on n_{12} , and $n_{11} - n_{22}$ in the region of relatively low shear rates. Higher shear rates cannot be examined, because parasitic gradients at the window surfaces lead to depolarization of the transmitted light.

2. A rectangular slit apparatus for the measurement as a function of shear rate or shear stress of the birefringence in the 1-3 plane.

Data on $n_{11} - n_{33}$ are obtainable at all shear rates from intermediate to extremely high. The lower limit is determined by the optical sensitivity of the chosen melt.

3. A capillary device with interchangeable dies for the measurement of the birefringence in the 2-3 plane.

This gives direct readings for $n_{22} - n_{33}$ in the intermediate range of shear rates, and tends to overlap the shear rate region covered by the previous two apparatuses. The upper limit to measurement is determined by depolarization effects, probably from the entrance or exit flows.

In the theoretical section, introduction is made to the now well-known molecular theories of polymer flow, based on a diffusion equation. A modification is made to the dumbbell to predict the ratio of the difference $n_{33} - n_{22}$ to $n_{11} - n_{22}$. The extension is based on the observation that segments of a molecule are rod-like and should have anisotropic diffusion coefficients. The experimental results are shown to be in accordance with the theoretical predictions of the ratio.

The validity of the stress-optical relation for steady shearing flow has been examined for a series of several different polymers with varying molecular weights and molecular weight distributions. In all cases, strong evidence was found for the stress-optical rule with a coefficient independent of molecular weight or molecular weight distribution. For systems, containing more than one phase, however, the rule does not hold, as might be expected.

A series of polystyrenes with narrow molecular weight distributions were measured to check the Rouse theory applied to the melt. The results agree with all other measurements on the same materials and indicate that J_e is proportional to M , as the theory demands, up to a molecular weight of about 10^5 and

thereafter levels off to a constant value of about $1.8 \times 10^{-5} \text{ m}^2/\text{N}$. The broad molecular weight polymers gave higher J_e values than the narrow molecular weight polymers, even when their molecular weights were higher than the critical molecular weight.

The superposition of the dynamic-mechanical quantities onto the steady shearing viscosity and the normal stress differences has been examined. The Cox and Merz relation ($\eta(q) \approx |\eta(\omega)|$) was found to hold, but more general relations were not found. Alternative to the Cox and Merz relation, linear relations between the above-mentioned quantities were constructed directly from experimental data. This device helped determine kernel functions which various theories suggest could simultaneously describe the viscosity and the normal stress behaviour. The *general* conclusion was that the kernels found were not in good agreement with any of the theories, nor was it possible to use, if accurate values were required, the same kernel for both the normal stresses and the viscosity function.

Finally, a study has been made of injection moulding, where it was shown how the experimental insight gained, could be used to predict orientation levels in moulded parts.

Samenvatting

Dit proefschrift behandelt stromingsdubbelebreking van polymere smelten. Bijzondere aandacht is besteed aan de eigenschappen bij stationaire afschuifstroming. Het onderzoek bestaat uit een experimenteel en een theoretisch deel. Het experimentele deel beschrijft de konstruktie van nieuwe apparaten voor de meting van stromingsdubbelebreking; deze werden door ons ontwikkeld, omdat ze niet commercieel verkrijgbaar zijn.

1. Een kegelplaatapparaat voor meting van de dubbelebreking en de uitdovingshoek in het 1-2 vlak.

Dit apparaat geeft waarden van n_{12} en $n_{11} - n_{22}$ als funktie van de snelheidsgradiënt bij relatief lage afschuifsnelheden. Hogere snelheidsgradiënten kunnen niet worden onderzocht, omdat het doorvallende licht in dat geval grotendeels door randeffekten wordt gedepolariseerd.

2. Een apparaat met een rechthoekige spleet voor het meten van de dubbelebreking in het 1-3 vlak als funktie van de snelheidsgradiënt of van de afschuifspanning.

Dit apparaat geeft $n_{11} - n_{33}$ van matige tot extreem hoge snelheidsgradiënten. De hoogste grens wordt door de optische eigenschappen van de smelt bepaald.

3. Een apparaat met verwisselbare capillairen voor het meten van de dubbelebreking in het 2-3 vlak.

Hiermee worden $n_{22} - n_{33}$ bij matige snelheidsgradiënten bepaald, tussen de gebieden die met de eerste twee apparaten kunnen worden gemeten. De bovengrens wordt bepaald door de depolarisatie, die bij de intrede of de uittrede wordt opgewekt.

In het theoretische deel wordt de dubbelebreking bij stroming van polymeren beschreven met behulp van de, nu welbekende, moleculaire theorieën op basis van een diffusievergelijking. Een modifikatie van het elastische haltermodel wordt gegeven, waarbij de verhouding $(n_{33} - n_{22})/(n_{11} - n_{22})$ kan worden voorspeld. De modifikatie is gebaseerd op de overweging dat de onderdelen van een polymere keten staafvormig zijn en daarom anisotrope diffusiecoëfficiënten moeten hebben. De experimentele resultaten zijn in overeenstemming met de theoretische voorspelling.

De geldigheid van de spannings-optische relaties voor stationaire (afschuif) stroming werd voor een reeks homopolymeren met verscheidene molekuulgewichten en molekuulgewichtsverdelingen onderzocht. In alle gevallen bleken de spannings-optische coëfficiënten konstant te zijn en onafhankelijk van het molekuulgewicht en de molekuulgewichtsverdeling. Bij meer-fasen systemen was de lineaire spannings-optische relatie, in overeenstemming met de verwachting, niet aanwezig.

De stromingsdubbelebreking werd gemeten aan smelten van een reeks polysty-

renen met nauwe molekuulgewichtsverdelingen om de Rouse theorie, toegepast op de smelt, te toetsen. De verkregen resultaten stemmen overeen met andere metingen aan dezelfde materialen. De kompliantie J_e is evenredig met M , zoals de theorie voorschrijft, tot een molekuulgewicht van ongeveer 10^5 ; daar boven wordt J_e konstant met een waarde van ongeveer $1.8 \times 10^{-5} \text{ m}^2/\text{N}$. De polymeren met een brede molekuulgewichtsverdeling gaven hogere J_e waarden dan de polymeren met een nauwe molekuulgewichtsverdeling, ook wanneer de molekuulgewichten hoger waren dan het kritische molekuulgewicht.

De dynamische glijdingsmoduli werden vergeleken met de viskositeit en de normaalspanningsverschillen, berekend uit stromingsdubbelebreking bij stationaire stroming. De Cox en Merz relatie (Eq. 5.5.5) voor de viskositeit werd bevestigd voor deze polymere smelten, maar meer algemene relaties voor normaalspanningsverschillen niet gevonden. Als alternatief voor de Cox en Merz relatie werden lineaire relaties tussen de bovengenoemde grootheden gekonstrueerd. Op deze manier werden functies bepaald voor de toetsing van enkele theorieën. De algemene konklusie was dat deze functies niet in overeenstemming waren met de theorieën, en ook bleek het onmogelijk om functies te vinden die zowel voor de viskositeit als voor de normaalspanningsverschillen toepasbaar zijn.

Ten slotte werd een studie gemaakt van het spuitgietproces, waarbij werd aangetoond, dat de verkregen inzichten kunnen worden gebruikt om het oriëntatieniveau van gegoten onderdelen te voorspellen.

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Levensloop

De schrijver werd in 1939 in Kensington (London, Groot Brittannië) geboren. Hij bezocht de Woodley Hill Grammar School, nu Forest School geheten, te Winkersley in het Graafschap Berkshire, van 1950 tot 1957.

Van 1957 tot 1960 bezocht hij de Universiteit van Bristol, Afdeling Wis- en Natuurkunde, waar hij de Bsc behaalde.

Na één jaar werkzaam te zijn geweest bij A.V. Roe te Manchester, werd de studie in 1961 aan het toenmalige College of Aeronautics in Cranfield, Bedfordshire, nu Cranfield College of Technology, hervat, waar hij in 1963 het diploma "Material Science", later in een MSc veranderd, bij Prof. Dr. D.W. Saunders behaalde.

Sindsdien is hij werkzaam bij het Centraal Laboratorium van de Nijverheidsorganisatie TNO te Delft, waar het hier beschreven onderzoek is uitgevoerd.

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1. Introduction

1.1 Preamble

The science to which this work is appended is termed rheology and rheology means the study of flow and deformation of liquids and solids with emphasis on the underlying physical processes.

Characteristic for solids is that they respond to a force by deforming, and, on removal of the force, by returning to their original shape. This type of response is termed elastic. Characteristic for liquids is that they deform and continue to deform as long as the force is present. This type of response is termed viscous.

The two definitions just given for viscous and elastic response represent two extremes of response to an external force. Materials do not always fall readily into one or the other of the above-mentioned categories. An additional parameter is needed to describe material response more fully. The extra parameter is time. As a general rule the faster the deformation the closer the response is to being elastic, the slower the deformation the closer the response is to being viscous. Slow and fast are factors relative to some natural time, τ , of the material. This natural time may be thought connected with the rates of spontaneous diffusion of its molecular and atomic constituents. For everyday fluids as water, the natural time is very short, of the order of 10^{-10} s¹⁾ and hence for most purposes is considered as being viscous. For a material such as glass, the natural time is very long, and consequently this material is bracketed as being elastic. Materials with natural times of the order of daily events (seconds, minutes, hours) are defined as being viscoelastic. The materials of this investigation fall into this class.

The forces on a material element can act internally (gravity, electrical and magnetic fields) or externally on the surfaces of the element. In the latter case the forces on the element are defined by the stress tensor p_{ij} ($i=1,2,3$). With an arbitrary coordinate system with base vectors $\underline{e}_1, \underline{e}_2, \underline{e}_3$, the force $\underline{f}_i$ on a unit surface of normal $\underline{e}_j$ is obtained by the relation:

$$\underline{f}_i = \sum_{j=1}^3 p_{ij} \underline{e}_j \quad (1.1.1)$$

As a consequence of the balance of angular momentum, the stress tensor is symmetric, i.e. $p_{ij} = p_{ji}$. The last result holds only in the absence of internal spin and in the absence of certain magnetic and electrical fields.

Simple shear flow is an important class of flow and forms the major subject in this work. Using a right handed coordinate system to define the flow, the usual convention is retained with: 1 - the flow direction; 2 - the direction of the flow gradient, and 3 - the neutral direction. If a particle in simple shear flow is given coordinates (ξ_1, ξ_2, ξ_3) at some time t_1 previous to the present time t then the present coordinate position (x_1, x_2, x_3) reads:

$$x_1 = \xi_1 + q(t - t_1)\xi_2 \quad (1.1.2)$$

$$x_2 = \xi_2 \quad (1.1.3)$$

$$x_3 = \xi_3 \quad (1.1.4)$$

where q is the shear rate and the macroscopic deformation is $s = q(t - t_1)$. Also present in simple shear flow is a shear stress p_{12} . This quantity represents a force in the flow direction but acting on a unit surface normal to the 2-direction.

The relationships between the stresses, the deformations and time is the essence of rheology: in the following section we begin with the linear theory.

1.2 Linear Viscoelasticity

The basic premise of the linear theory is found in the Boltzmann superposition principle²). The following form is convenient:

$$p_{12}(t) = \int_{-\infty}^t q(t_1)G(t - t_1)dt_1 \quad (1.2.1)$$

where $p_{12}(t)$ is the shear stress at time t , $q(t_1)$ the shear rate at time t_1 , and $G(t - t_1)$ is a time-dependent modulus which decreases as the interval $(t - t_1)$ increases. Physically, the principle relies on the linear additivity of the stress increments from past deformations. Each deformation $q(t_1)dt_1$ at some time t_1 in the past contributes to the stress at time t by an amount $G(t - t_1)q(t_1)dt_1$. The sum over all past deformations defines the present state of stress. Similar formulations can be made for deformations other than simple shear.

The steady shear viscosity defined as the ratio of the equilibrium shear stress to the constant shear rate q follows immediately:

$$\eta = \int_0^{\infty} G(\tau)d\tau \quad (1.2.2)$$

The transformation $t - t_1 = \tau$ has been made for convenience. It is possible to construct an expression similar to 1.2.1 but giving the deformation as a function of the past stress and a compliance $J(t - t_1)$. The time-dependent modulus G and the compliance J are interrelated by³):

$$\int_0^t G(t_1)J(t - t_1)dt_1 = t \quad (1.2.3)$$

In this linear theory the material shows an interesting elastic property: the material recovers a part of the impressed deformation when the force is removed. For simple shear flow the "shear recovery" is defined as the total recovery at infinite time after cessation of steady shearing:

$$s_{\infty} = J_e \eta q \quad (1.2.4)$$

where J_e is called the steady shear compliance.

$$J_e = \frac{1}{\eta^2} \int_0^{\infty} \tau G(\tau)d\tau \quad (1.2.5)$$

So far we have only considered steady shearing; time-dependent motions are also important and a particularly important one is obtained by sinusoidal stressing with deformations of small amplitude. In general, the stress is out of phase with the strain. However, the stress can be decomposed into two com-

ponents, one in-phase and one 90° out of phase with the movement. Division of the amplitudes of these stress components by the strain amplitude defines a complex modulus as consisting of an in-phase component and an out-of-phase component. The in-phase component or storage modulus is termed G' and represents the stored energy, the out-of-phase component or loss modulus is termed G'' and represents the dissipated energy. The phase angle between the in- and out-of-phase components is given by $\tan \delta = G''/G'$, and the ratio of the peak stress to the peak strain is called the absolute value of the dynamic modulus $|G^*|$:

$$|G^*| = [G'^2 + G''^2]^{\frac{1}{2}} \quad (1.2.6)$$

Equivalently, the results of dynamic experiments can also be expressed through the J 's. It is also possible to define a real η' and an imaginary η'' component of viscosity from the moduli G'' and G' :

$$\eta' = G''/\omega \quad (1.2.7)$$

$$\eta'' = G'/\omega \quad (1.2.8)$$

where ω is the applied circular frequency. The dynamic moduli are expressed in terms of a continuous distribution of relaxation times since in practice it is found that a single relaxation time is insufficient to describe the behaviour of most materials.

$$G' = \int_{-\infty}^{\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d(\ln \tau) \quad (1.2.9)$$

$$G'' = \int_{-\infty}^{\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d(\ln \tau) \quad (1.2.10)$$

where $H(\tau)$ is habitually called the relaxation time spectrum; an unfortunate name since $H(\tau)$ has the dimension of a modulus and does not only convey the meaning of a statistical frequency. All the above relations can be developed from the Boltzmann principle³⁾. The conditions to be met are those of linearity: a change of amplitude of the applied deformation may not effect the derived moduli. It appears that these requirements are always met with polymer solutions and pure melts, even at rather large strain amplitudes: many other liquid systems which are structured (e.g. clay suspensions, certain soaps⁴⁾) and most solids - including some metals⁵⁾, do not show linearity except at extremely low deformations.

1.3. Normal Stresses in Simple Shear Flow

Associated with the shear stress in simple shear flow are stresses acting perpendicular to the normal surfaces formed by the coordinate axes. According to classical fluid mechanics these normal stresses, p_{ii} , are all equal to the local pressure and hence normal stress differences $p_{ii} - p_{jj}$ (no summation over the indices) are zero. For non-Newtonian fluids such as polymer melts and solutions at high shear rates, these normal stress differences do not

vanish. As a result, the cross of the principal axes of stress is inclined with respect to the stream lines. Its position can be described by a single angle for which the one smaller or equal to 45° is chosen*.

To explain deviations from 45° , as found by early workers, at the turn of the century postulations were made that elastic liquids of the type proposed by Maxwell, should possess unequal normal stresses (see Section 1.4). These early ideas seem to have been lost and at a later date it was left to K. Weissenberg⁶⁾ to devise the first apparatus for the measurement of the normal stress differences.

At the present time, extensive measurements of normal stresses have been carried out on polymer solutions. Polymer melts have not been so extensively investigated and other non-Newtonian fluids hardly at all.

The Boltzmann principle of the previous section does not predict unequal normal stresses in shear flow. Lodge⁷⁾ overcame this problem by using a description of strain that was applied earlier by Weissenberg in his non-linear theories of elasticity. Lodge adapted this description for a description of liquid behaviour.

In developing his theory, he used a particular model: the temporary network model for concentrated solutions and melts. However, the results are probably of more general validity. He proposed the following equation of state:

$$p_{ij}(t) = \int_{-\infty}^t N(t - t_1) \frac{dx_i}{d\xi_m^1} \frac{dx_j}{d\xi_m^1} dt_1 - P_0 \delta_{ij} \quad (1.3.1)$$

where $N(\tau)$ is a "memory function" and the usual summation has been applied to repeated indices; P_0 is a hydrostatic pressure, and x_i and ξ_i^1 denote the coordinates of the positions occupied by particles at the time of observation t and at a previous time t_1^1 , the x_i being expressed as functions of the ξ_i^1 . The physical basis for the above model is the same as that of the Boltzmann principle: the linear addition of past deformations coupled with a time-dependent modulus gives the present state of stress. However, non-linear terms in the strain tensor must be taken into account for the calculation of the normal stresses.

For the case of steady shear flow given by equations (1.1.1) to (1.1.3) there has been obtained:

$$p_{12} = q \int_0^\infty N(\tau) \tau d\tau \quad (1.3.2)$$

$$p_{11} - p_{22} = q^2 \int_0^\infty N(\tau) \tau^2 d\tau \quad (1.3.3)$$

$$p_{22} - p_{33} = 0 \quad (1.3.4)$$

These equations show that for steady shearing the shear stress is proportional to the gradient q ; the normal stress difference $p_{11} - p_{22}$ is proportional to the square of the gradient and the normal stress difference $p_{22} - p_{33}$

*The reader is reminded that for Newtonian fluids the principal stresses lie at 45° to the flow direction.

should be zero. The state of affairs where the viscosity is independent of the gradient (the so-called Newtonian region) and the normal stress differences proportional to the square of the gradient leads to the term second order region. Classical (i.e. linear) viscoelasticity has also a constant viscosity independent of the gradient.

If $G(t)$ vanishes at infinite time, $N(\tau)$, $G(\tau)$ and $H(\tau)$ can be related⁸⁾:

$$N(\tau) = - \frac{dG(\tau)}{d\tau} = \int_0^\infty \frac{H(s)}{s^2} e^{-\tau/s} ds \quad (1.3.5.)$$

In subsequent chapters equations 1.3.2. and 1.3.3. are expressed in terms of $H(\tau)$ instead of $N(\tau)$.

A set of equations can be derived from this theory relating the orientation angle χ_m of the stress tensor in steady shear flow, the recovery s_∞ after steady flow, and the phase angle δ in oscillatory shear:

$$\cot 2 \chi_m = \frac{P_{11} - P_{22}}{2 P_{12}} = J_e \eta \dot{\gamma} = J_e P_{12} \quad (1.3.6)$$

$$s_\infty = \cot \delta = \cot 2 \chi_m \quad (1.3.7)$$

where δ is to be evaluated at a low frequency equal to the shear rate at which the corresponding steady shear flow experiment is carried out.

1.4 Flow Birefringence

Most molecules are optically anisotropic. When the molecules in an assembly are completely randomly distributed then the assembly behaves as an isotropic medium. If the assembly can be brought either partially or fully into a state of orientation by any means whatsoever, then double refraction (birefringence) will occur. Orientation in liquids may be achieved by the application of electrical fields (Kerr effect), magnetic fields (Cotton-Mouton effect), acoustic waves (Lucas effect) or by flow (Maxwell effect). The general problem of double refraction including flow birefringence, was considered by Peterlin and Stuart⁹⁾. Other reviews, discussing particular and general aspects of flow birefringence, have also appeared from time to time¹⁰⁻¹⁶⁾. The most recent account with particular emphasis on macromolecular fluids has been given by Janeschitz-Kriegl⁸⁾.

Definition of the terms extinction angle and birefringence

The liquid is viewed through crossed polarizing devices so that light travels perpendicularly to both the stream lines and the velocity gradient. The field appears dark when the liquid is at rest. Under the influence of the hydrodynamic forces the fluid becomes optically biaxial, i.e. it possesses three different principal axes with three different principal refractive indices. One of these axes coincides with the direction of the light beam and the other two lie in the plane of observation. The field now appears dark or light depending on whether the orientation of the crossed polarizers corresponds with the orientation of these two principal axes or not.

The extinction angle χ is defined as the smaller of the two angles between

de die twee van de indicatrix

the shearing planes and the vibration planes of the polarizers, which give rise to the dark field. According to this definition, χ lies between 0° and 45° .

When linearly polarized light of wavelength λ (in vacuo) passes through a length d of doubly refracting medium it is resolved into two linearly polarized components one along each principal axis in the viewing plane. These components emerge with a phase difference δ (radians) which is given by $\delta = 2 \pi d \Delta n / \lambda$. In this formula $\Delta n (= n_I - n_{II})$ is the difference between the principal refractive indices in the viewing plane, which we call the birefringence. The principal refractive index n_I is, in accordance with the previously given definition of the extinction angle, taken from that principal axis which points between the flow vector and the gradient vector. The sign of the birefringence is positive or negative as n_I is greater or less than n_{II} .

Historical background of the stress-optical effect

The discovery of artificial double refraction by stress was made by Brewster in 1816¹⁷⁾. He found that a plate of glass under simple tension acquired the properties of a uniaxial crystal. Further experimentation on solids carried out by Neumann and later by Maxwell^{18,19)} culminated in the formulation of stress-optical laws before the discovery of double refraction induced by flow. Formulated in the terms of stress these laws are:

- 1) At any point in a stressed transparent solid the axes of polarization of light passing through the solid are parallel to the directions of the principal stresses in the plane of the wave front at that point.
- 2) The differences of the velocities of the two oppositely polarized rays at the point is proportional to the difference of their two principal stresses, and is independent of stresses perpendicular to the wave front.

In simple shear the refractive index tensor has components n_{ij} corresponding to the stress components p_{ij} . Explicitly, the non-zero components are n_{11} , n_{22} , n_{33} and n_{12} . The birefringence Δn in the 1-2 plane and the extinction angle χ are formally related to the stress components by:

$$\Delta n \sin 2\chi = 2 n_{12} = 2 C p_{12} \quad (1.4.1)$$

$$\Delta n \cos 2\chi = n_{11} - n_{22} = C(p_{11} - p_{22}) \quad (1.4.2)$$

where C is called the stress-optical coefficient.

The first published, qualitative, observations on flow birefringence were made by Mach²⁰⁾ in 1873 on viscous substances such as Canada Balsam and strong metaphosphoric acid. Maxwell²¹⁾ described in 1874 a concentric cylinder apparatus used by him in earlier experiments on Canada Balsam. The first real attempts to get quantitative measurements and a theory for streaming double refraction were made by Kundt²²⁾. According to his view, each elemental volume is subjected to tensile and compressive stresses along two directions which are mutually perpendicular and inclined at 45° to the lines of flow. These stresses are proportional to ηq where η is the viscosity and q the velocity gradient.

Kundt assumed, thus, stresses produce double refraction in a liquid just as they do in a solid. The optic axes were assumed coincident with those of stress. According to the ideas at that time, χ should be 45° and any departure from this value was an unexplainable anomaly. Several such cases were found. An attempt to explain such departures was first made by Schwedoff²³⁾. He rejected the possibility that the optic axes do not coincide with the axes of stress and concluded that the latter do not always lie at 45° . This amounts in modern terms to the view that additional forces vectored in the gradient and flow directions are induced by the flow and that these normal forces are not equal. Moreover, Schwedoff deduced a relation between χ and a quantity related to the (fugitive) elasticity of the fluid as defined by Maxwell²⁴⁾. Later, Nantonson²⁵⁾ obtained the modern looking equation:

$$\cot 2\chi = q\tau \quad (1.4.3)$$

As will be seen later, first in Fig. 2.6b, this equation gives a qualitatively correct description of the so-called extinction angle curve: starting at 45° to the flow direction, this angle decreases, in general, monotonically with increasing shear rate. (At the same time, birefringence Δn increases continuously from zero, and, sometimes, shows a tendency of saturation within the accessible range of shear rates, cf. e.g. Fig. 2.6a).

Thus, the initial ideas concerning double refraction in streaming flow were basically that the birefringence was caused by stresses just as in solids. Later, alternative proposals were made¹⁴⁾ that the movement and reorientation of the constitutive particles should be considered^{14,26)} and, further, that a distinction should be made between rigid and flexible particles. This is, essentially, the modern standpoint. Advancing swiftly to more recent times, Lodge was apparently the first to suggest that for sufficiently flexible, amorphous, polymers in solution a stress-optical relation, as defined at the beginning of this section, should hold. He substantiated his proposals by re-examining²⁷⁾ some old results of Signer, amongst others. Re-appraisal of these earlier investigations showed that the quantity $\Delta n \sin 2\chi/p_{12}$ where p_{12} is the shear stress, was essentially independent of the gradient even though χ showed considerable deviations from 45° . As the measurement of normal stresses was not thought of at the time of the original measurements, it was not possible to make direct comparison of the extinction angle χ with the orientation of the stress axes. Lodge was able to show, using his network model, that the coefficient of the stress optical law should be the same as that for crosslinked elastomers of the same polymer. As is known, for this latter case, the coefficient is independent of the concentration of effective chains and of their lengths²⁸⁾. Philippoff and co-workers^{29,30a)}, in following up these proposals, could show that in some cases the quantity $\Delta n \sin 2\chi/p_{12}$ was constant over many decades of the shear stress, as theory required, independent of gradient, concentration and molecular weight of the polymer. He was able to demonstrate for some solutions that the optical and mechanical "extinction" angles had the same value^{30b)}.

Experimentally, the bounds of validity of the stress-optical relation have not yet been fully defined. Consequently, the usefulness of the relation in

determining stress distributions in complicated flows of viscoelastic materials cannot be guaranteed as yet. We expect deviations to occur from the simple linear stress-optical relation when motions are unsteady or the stresses are too high. Moreover, there will be qualitative differences between diluted solutions and melts.

With diluted solutions, high shear stresses (i.e. greater than 10^4 N/m²) are not usually attainable. We do not expect deviations to occur on this account. It appears with these fluids that the stress-optical relation holds to a good approximation in oscillatory experiments. In one case of a high molecular weight material, deviations between the stress and optical phase angles first occur at frequencies about two decades higher than the reciprocal natural time of the system³¹). Therefore we believe the relation to be of general applicability as long as the solutions are amorphous and the molecular weights are sufficiently high.

Few results have been established for melts; the stress-optical relation for steady flow is, in part, the subject of this study. It is known that, in oscillatory testing near the glass temperature T_g , the stress and the birefringence can be out-of-phase with one another as well as with the imposed deformation³²). In the true melt region (at least 40 °C above T_g), however, no results appear to have been published. We may, however, expect that for sufficiently fast changes the stress-optical relation will not hold in principle. How fast these changes should be with respect to the materials times in order to obtain serious deviations from this law, remains open. One may expect that deviations occur at frequencies at which the glass transition is reached. However, there is one example of a non-steady flow for which the stress-optical relation has been investigated. The case in mind is melt spinning, where very high transient stresses can be generated. For some systems the birefringence remains linear in the stress over the complete measurement range (up to 10^7 N/m²), for others the birefringence reaches saturation³³). Deviations from linearity do not occur below stresses of the order of 10^6 N/m². This has a parallel in the behaviour of rubbers where a linear stress-optical relation also holds for stresses up to this order²⁸). In the case of rubbers it is known that the deviations are a function of the degree of crosslinking³⁴). The higher the degree of crosslinking the lower the stress level at which deviations from linearity become significant. In some cases²⁸) of low degree of crosslinking the linearity is retained up to 7×10^6 N/m². In rubbers the origin of the non-linearity at the higher stresses is thought to be the length of the chains between the crosslinks being too short for the applicability of the ideal Gaussian chain model³⁴) (see Section 4.1).

The present author does not believe that these points will be of serious matter for shearing flow in normal solutions and melts since (deviatoric) stress levels do not ever greatly exceed 10^6 N/m² even during the injection moulding cycle. Moreover, the polymers in normal use have higher molecular weights (longer chain lengths) than the materials used ordinarily in spinning.

1.5 Scope of the Investigation

The major concern of this investigation is the experimental use of flow birefringence to measure and characterize molten polymers of the type that are

of industrial interest; only a few model fluids will be used. Owing to the relative simplicity of the methods of flow birefringence it has been found possible to develop instruments which can completely define the anisotropy of the refractive index tensor in steady shear flow. Specifically, direct determinations of the quantities n_{12} , $n_{11}-n_{22}$, $n_{11}-n_{33}$ and $n_{33}-n_{22}$ will be reported. Next, experimental evidence will be presented, as far as possible, for the validity of the stress-optical law as defined in Section 1.4. The obtained optical quantities will then be used for the evaluation of a few molecular theories which predict relations between molecular weights and J_e . Next, the data found from steady shearing will be used to examine theoretical relations between the stress tensor in steady shear flow and quantities which can be obtained from (small deformation) measurements of the dynamic moduli. The interest being here the perhaps distant possibility that dynamic measurements could predict even non-linear steady flow behaviour. Finally, a study has been made of a case where the developed methods for the measurement of the birefringence in steady flow could be used in practise. The example chosen is injection moulding where in some cases the degree of molecular orientation is predictable in the ejected parts; the importance being that some mechanical properties are extremely sensitive to the orientation frozen in during the injection cycle.

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2. Apparatus

APPARATUS

2.1 The Cone-and-Plate Apparatus

The first apparatus to be built was made to measure the flow birefringence in the 1-2 plane. The quantities measured are the birefringence Δn , and the orientation angle of the ellipse to the stream lines. The choice fell on a cone-and-plate device in view of the experience that this geometry has been proven to be more useful in viscometry of elastico-viscous fluids like polymer melts than the co-axial cylinder type. Amongst other advantages, filling is easier.

Figure 2.1 gives a schematic representation. The conical surface is formed by the inner end-surface of disk C, which is stationary. The plane surface is on disk D, which forms the rotor. Axle A on which disk D is mounted, fits into a combined thrust and axial bearing, B_1 , and is driven by gear box G. The gear box is itself driven via a set of interchangeable reduction gears, by an electronically controlled variable speed motor (Contraves, Zürich). With a cone angle ϵ of $1^\circ 8'$ and a disk diameter of 50 mm, the range of shear rates is from 10^{-4} to 10^2 s^{-1} .

The units B_1 , D and C fit into a cylindrical block B_2 which is surrounded by the heating elements H. The temperature is controlled by a thermocouple inserted into the back of block B_2 .

Fig. 2.1 Schematic diagram of cone-and-plate apparatus and auxiliary equipment: (C) cone; (D) disk (i.e. plate); (B_1) bearing; (A) axle; (G) gear box; (P, A) polarizer and analyzer (polarizing sheets); (T) tube-shaped window holder; (S) drum scale. The remaining symbols are explained in the text.

The light beam enters from below through polarizer P and passes tube T which serves as a holder for the lower window. The window is indicated by a half sphere on top of tube T. Here the light beam enters the gap between plate D and cone C in a radial direction. The upper window is not shown in Fig. 2.1. Inside parts C and D there is, besides the window, also a prismatic mirror which reflects the light beam so that it leaves the unit in a horizontal direction.

Details of this arrangement are shown in Fig. 2.2. From this figure it is seen that a relatively large chamber which is symmetric with respect to the axis of revolution, is inside parts C and D. In this chamber part E is fitted. It is rigidly connected with the stationary conical part C. Both parts are pressed with the aid of cover Z against disk K. Disk K, which rests on bearing B₁, ensures the correct distance between the parts D and C, so that the geometrical apex of the cone is exactly on the geometrical plane of the front surface of D.

Inside part E there is cylinder V, which can be rotated about the incident light beam. It contains the upper window W₂ and the reflection prism M. Q₁ is a handle, the function of which will be described later. F is a bore into which the filling device fits. (A rod of material is melted in a reservoir and pushed into the unit with the aid of a piston.)

The glass used for both the windows and the prismatic mirror (optical glass BK 7, Schott and Gen. (Borfe)) has a low coefficient of cubical expansion ($\alpha = 2.3 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$) and a low homogeneous residual birefringence. Its index of refraction is $n_d = 1.5163$ and its dispersity between the C and F lines is 0.0081. The body of the unit as well as parts C, D, E, and V are made of nitrided steel.

Fig. 2.2 Detailed scale drawing of heart of cone-and-plate system: (C) cone; (D) plate; (W₁, W₂) windows, (M) reflection prism. The action of the other parts is described in the text.

The windows, W₁ and W₂, are hemispherical. Parallel flat surfaces are ground vertically to the equatorial plane into the glass body of each window. These surfaces fit between the jaws on top of the holders (parts T and V). In

this way, the windows must rotate together with the holders. Near the jaws the window rests with its equatorially cut surface on the flat area of the holder top. To prevent the spherical surface from acting as a lens, a very small plane surface is ground on top of the window. The surface of this is also polished.

It is seen from Fig. 2.2 that the light beam passes only through one side of the ring-shaped gap. In fact, if it were not led out near the centre, the birefringence on one side would be compensated by the birefringence on the other side of the centre.

Returning to Fig. 2.1, the light beam is followed on its horizontal path. It passes lens L and analyzer A before it reaches the ocular which is only schematically drawn. Part R remains to be described. It consists of a horizontal bar which is soldered to nave N, and a vertical beam which carries on its upper end the telescopic tube for the ocular. It is seen from the drawing how lens L and analyzer A are mounted on part R. Between L and A there are two slide channels: one in a vertical, the other in a horizontal direction. These slide channels serve for the insertion of a compensator in the correct attitude. The part designated U consists of two parts, U_1 and U_2 , which are connected by two shafts fitting into horizontal bores in part R. The spiral springs on these shafts are counteracted by screw J. In this way part U can be moved in both directions by turning screw J. U_2 contains two holes in which handles Q_1 and Q_2 are fit. These handles are connected with parts T and V.

Now the working of the apparatus can be described. For the determination of the extinction positions, polarizer P is set parallel with the plane of incidence of mirror M. In this way, the mirror is extinguished when analyzer A is put into the crossed position. This adjustment is carried out with the rotor at rest. With turning rotor the melt in the gap is birefringent. To seek the extinctions, part R is turned around the axis of the incident light beam. Due to the action of handle Q_1 , mirror M is turned together with part R so that the relative positions of the polarizer and mirror are maintained. The positions of dark field are read from drum scale S. The function of Q_2 is to let window W_1 rotate with window W_2 . It appears that in this way occasional strains in the windows are released. The angular positions of the flow lines on the arbitrary scale S on the stand is not known better than to within 4° owing to small variations in the clamping position in day-to-day use. To find the true extinction angle the motor is normally reversed and a second extinction is found. The two extinction positions are symmetric with respect to the flow lines and the true extinction can then readily be found.

For the determination of the birefringence, polarizer and analyzer are rotated 45° in their fittings, and the compensator is inserted in the suitable slide channel to give subtraction with the combined birefringence of polymer melt and reflection prism. The latter value can be calculated from the Fresnel equations for total reflection. The formula reads²⁾:

$$\tan(\phi/2) = \frac{\cos u (n^2 \sin^2 u - 1)^{\frac{1}{2}}}{n \sin^2 u} \quad (2.1.1)$$

where ϕ is the phase difference due to the mirror, u is the incident angle of light to the plane of mirror, and n is the refractive index of glass relative to air. The theoretical value of the path difference caused by the prism is

60 μ in green (548 μ) light. Experimentally the path difference due to the mirror is measured with the rotor still. The values found are in the range 56 μ to 64 μ . This difference between the experimental and theoretical is probably ascribable to slight setting faults in the prism. If the angle of incidence u were increased from 45° to 46° , then the theoretical value would increase to about 64 μ .

2.1.1 Limitations of Cone-and-Plate Apparatus

Boundary Conditions

One great difference with conventional cone-and-plate devices is contained in the boundary conditions. Normally, the boundaries are formed by the metal surfaces $\theta = \pi/2$ and $\theta = \pi/2 - \epsilon$ (spherical polar coordinates), and there is a free boundary with the atmosphere. In the present case, in addition to the metal boundaries at $\theta = \pi/2$ and $\theta = \pi/2 - \epsilon$, there are cylindrical metal boundaries at $r = r_1$ and $r = r_2$. This means deviations from the assumed flow pattern at or near these boundaries. For small values of ϵ it is known that the flow field in a symmetrically adjusted cone-and-plate is given by the equation^{3,4}):

$$V_\phi = \omega \frac{r \cos \theta}{\sin \epsilon} \quad (2.1.2)$$

where ω is the angular velocity of the cone about its axis. We now assume that the actual cylindrical boundaries at r_1 and r_2 may be replaced by spherical ones in the case of small ϵ . The requirements now has to be made that $V_\phi = 0$ at $r = r_1$ and at $r = r_2$ in order to satisfy the condition of no slip at the metal boundaries. The exact solution for this problem could be sought by trying to solve the vector Laplace equation in spherical polar coordinates which governs the slow motion of viscous liquids. In attempting this, the author was unsuccessful. To obtain some estimate for the expected deviations of the flow field from the flow pattern undisturbed by the side walls at r_1 and r_2 the flow was likened to the flow in a rectangular duct, one large side wall of which is moving parallel with the channel with a constant speed V_0 . This may be justified by the intuitive consideration that errors induced by the metal surfaces at $r = r_1$ and $r = r_2$ will only seriously effect the flow at radial distances from r_i of the order of the gap between the cone and the plate at r_i . The gap is ϵr_i where ϵ is the angle between the cone and the plate. The gap is small compared with the local radius and so we do not expect the curvature of the system to influence the flow field calculations seriously.

The sides of the duct are given by the cartesian coordinate surfaces $z = 0$, $z = b$, and $y = 0$, $y = a$; the flow field is of the assumed form $V = [V(z,y), 0, 0]$ with $V(z,a) = V_0$ and $V(z,0) = V(0,y) = V(b,y) = 0$. The error estimate is only made for Newtonian liquids.

Since the conduit is closed, there can be no pressure gradient in the flow direction, x . The equation of motion for slow flows then has the simple form:

$$\frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xz}}{\partial z} = 0 \quad (2.1.4)$$

With the given assumption that no transverse flow occurs ($V_y = 0$) we have for Newtonian liquids with viscosity η :

$$P_{xy} = \eta \partial V_x / \partial y \quad (2.1.5)$$

$$P_{xz} = \eta \partial V_x / \partial z \quad (2.1.6)$$

The equations of motion found by substitution of (2.1.5) and (2.1.6) in (2.1.4) is the Laplace equation:

$$0 = \frac{\partial^2 V_x}{\partial z^2} + \frac{\partial^2 V_x}{\partial y^2} \quad (2.1.7)$$

The solution for V_x with the given boundary conditions is known as a series of eigen functions which conveniently form a Fourier series. A detailed discussion on this is given by Morse and Feshbach⁵).

The solution for the velocity distribution reads:

$$V_x = \frac{4V_0}{\pi} \sum_{n \text{ odd}} \frac{1}{n} \sin \frac{n\pi z}{b} \frac{\sinh \frac{n\pi y}{b}}{\sinh \frac{n\pi a}{b}} \quad (2.1.8)$$

This result is also quoted by McKelvey⁶). This expression is now used to estimate the possible errors.

A) The velocity gradient dV_x/dy

Light passes through the system in the z direction. The velocity gradient dV_x/dy is chiefly responsible for the birefringence. Seen in the microscope are the metal surfaces $y = 0$ and $y = a$ of the rotor and stator. We are mainly interested in the central region $y = \frac{1}{2} a$, as this corresponds to the centre of the optical image and is therefore the most convenient for observation. For this central region, an average value of the velocity gradient dV_x/dy over the z coordinate is first calculated, in order to find the effect of the boundary surfaces at $z = 0$ and $z = b$. We find:

$$\left\langle \frac{\partial V}{\partial y} \right\rangle = \frac{8}{\pi^2} \frac{V_0}{a} \sum_{n \text{ odd}} \frac{x}{n} \frac{\cosh xn/2}{\sinh nx}, \quad x = \frac{\pi a}{b} \quad (2.1.9)$$

For the cone-and-plate in question $b = 10$ mm and (a) varies from 0.3 to 0.5 mm. For calculation the latter value was used as it leads to more pessimistic estimates of the errors and thus may give an upper bound to them (the largest value of the depth to breadth ratio is involved). The above series is known to converge slowly. Machinal computation is the only practical method of evaluation. To this end use was made of a Bull-General Electric computer type GE-265. After fifty terms the calculated average gradient was constant at 97.79 % of the nominal value, V_0/a . Calculation was stopped after 100 terms. The error in this average velocity gradient is thus less than 2.3 %.

To give an impression of the variation of the velocity gradient in the 1-2 plane from the nominal gradient, Fig. 2.3 was prepared. The average gradient in the field of view was calculated as a function of the distance between the still boundary surface ($y = 0$) and the moving boundary surface ($y = a$). As can be expected very near the moving boundary surface the average gradient shows important deviations from the nominal value, here taken as 1 s^{-1} . From the figure it can be seen also that the position of closest agreement with the nominal gradient lies at about two thirds of the distance between the still and the moving boundaries. Taking $\pm 2\%$ as acceptable for the deviation of the average shear gradient from the nominal gradient, Fig. 2.3 indicates that measurements should be carried out between 0.53 and 0.76 of the distance between the still and the moving boundaries.

B) The parasitic velocity gradient dV_x/dz

This gradient differs considerably from zero only near the small side walls in which the windows are placed. Its maximum value is situated on the windows, i.e. at $z = 0$ and at $z = b$. Figure 2.4 has been prepared to show the variation of this parasitic gradient on one of the windows as one progresses from the still boundary surface, at $y = 0$, to the moving boundary surface at $y = a$. Near the still metal boundary the parasitic gradient is zero; in the middle it takes a value equal to the nominal value of the principal gradient dV_x/dy . It is infinite at the moving boundary. In connection with the observations made at the end of paragraph A) it is useful to see how fast the parasitic gradient dV_x/dz dies on moving from the window surface. Machine calculations based on equation (2.1.8) indicated that at 0.5 mm from the window the parasitic gradient in the centre of the field of vision had dropped to 8.6 % of its value at the window and at 1 mm to 0.01 % of the latter value. Figure 2.5 shows the course of the parasitic gradient as one progresses from one window to the other in the direction of the light beam. The influence of this gradient is such that, in the centre of field of view it induces on the window surface an optical effect equal to the birefringence ($n_{11} - n_{33}$) of the principal gradient*. This helps us to estimate the effect of the parasitic gradient on the measured quantities.

If the birefringence is small, contributions to it can simply be added in a vector diagram. Under these circumstances one obtains the following results: for χ close to 45° the disturbances at the windows will decrease the limiting birefringence by about 2% and increase the departure of χ from 45° by about the same amount. For χ is this completely unimportant and the error is acceptable for Δn . When the extinction angle is close to the stream direction ($\chi \sim 0$) the birefringence is hardly changed and again χ will be about 2 % too small. This result holds for the central plane ($y = a/2$) and was obtained from the data shown in Fig. 2.5 and from the course of the shear rate in the 1-2 plane. The errors due to the disturbances caused by the boundaries at $r = r_1$

*This birefringence is the Δn value measured in the 1-3 plane and is related to $p_{11} - p_{33}$. It is only measureable if the large side walls of the channel are transparent. Cf. Chapter 2.2.

and $r = r_2$ are thus acceptable within the approximation chosen. The actual apparatus has certain features which make the given calculations only rather rough. The windows are not fully flush with the metal boundaries at $r = r_1$ and $r = r_2$. They are sunk by about 0.2 mm. Moreover, the corners of the rectangular cross-section are not infinitely sharp. These complications cannot be properly taken into account.

Apart from the effects just mentioned, the disturbances at the windows cause depolarization at high gradients and as a result further measurement becomes impossible. It usually appears that depolarization occurs at a shear stress of about 10^4 N/m² or a little higher. The determining factor is not so much the relative magnitude of the parasitic birefringence, but its absolute magnitude. Light through a stack of randomly orientated plates can be extinguished between polarizing devices only, when the path differences of each plate are very small. When these path differences are not small, extinction is not possible, except when the plates are equally directed. Thus the limiting conditions under which the cone-and-plate device will give measurements are determined by magnitude of the gradients and by the nature of the material under study.

Fig. 2.3 The average value of the principal shear gradient evaluated between the windows, given as a function of the distance y/a between the still and moving boundaries.

Fig. 2.4 The parasitic gradient at the window, given as function of the distance between the still and moving boundaries. The principal gradient is nominally, 1 s^{-1} .

Fig. 2.5 The parasitic gradient in the central place as a function of the distance between the windows. The nominal gradient is 1 s^{-1} .

It should always be possible to measure at high shear stresses with optically weak materials if their extinction angles remain close to 45° . On the other hand, an optically strong material should be equally measureable at high gradients if it readily orientates in the flow field, i.e. approaches the orientation of the birefringence caused by the parasitic gradient.

2.1.2. Thermal Stability

All experimental work at elevated temperatures is bounded by the thermal stability of the substance concerned. We can class materials in two groups. The first group spontaneously change or degrade with or without an incubation period. PVC is an example. For this group of materials the cone-and-plate apparatus is at a disadvantage since filling and cleaning are time consuming.

The second group contains materials which are susceptible to attack from the environment. This is generally the oxygen in the atmosphere. Polyolefins are examples here. Against this attack the present cone-and-plate apparatus has great advantages over other cone-and-plate apparatuses: the material is totally enclosed by the metal surfaces. As an added precaution, material obtained from granulate or flocculated suspensions can be pre-moulded under vacuum in order to minimize a possible source of oxygen during the preparatory stage. In order to test the thermal stability of a member of this group and to determine the allowable measurement period, a 24 hours' test was carried out for a sample of high density polyethylene at the unusually high temperature of 240°C^* . If exposed to the atmosphere at this temperature, the given polymer would turn brown within a few minutes and char completely within two hours. At regular intervals during the 24 hours' period, the birefringence and the extinction angle were measured; Figs 2.6a and b show the obtained results, which also may serve as an example of the type of measurements, which can be obtained with the described apparatus. For the birefringence, only very small changes were found: a slight increase with time in the region of low gradients. Figure 2.6b shows the results obtained for the extinction angle. Here the changes are clearer: within the first hour nothing happens; after three hours the extinction angle has decreased and continues to decrease during the whole 24 hours' period. The greatest changes occur at the lowest shear gradients.

Normally, measurements are carried out at much lower temperatures. A temperature of 200°C is quite normal for rheological experiments on this type of material. It was concluded that it would normally be safe to measure at 200°C on the same sample for three or four hours. Nevertheless, when it was necessary to measure on a polymer for this length of time, "degradation" was checked by a repeat of the measurements made at the beginning of the interval.

*No extra stabilizer was added to that possibly present in the granules.

Fig. 2.6a Example of birefringence measurements obtained with the cone-and-plate apparatus during a 24 hours' test. The material is a high density polyethylene (Marlex 6050) and the temperature is 240 °C. The example shows the good stability of the material when examined by this apparatus.

Fig. 2.6b The extinction angle χ accompanying Fig. 2.6a. The extinction angle is seen to be more sensitive to degradation effects than the birefringence.

2.2 The Slit Apparatus : Measurements in the 1-3 Plane

The use of slit and capillary devices for the measurement of birefringence effects extends back prior to polymer research⁷⁾. Previous investigations were in the main concerned with non-polymeric liquids such as V_2O_5 sols⁸⁾ and experiments were carried out at or near room temperature. Work of this type was carried out in the years before the second world war in order to obtain qualitative information with streaming birefringence in the 1-3 plane. It was considered a great disadvantage that with slits and capillaries the optical effect is an average quantity over the flow field. For this reason, quantitative interpretation was considered impossible^{7,8)}. Unaware of this historical back-

ground, the present author could show that the averaging is very specific and with a few restrictions, quantitative values of the difference $n_{11} - n_{33}$ at the large slit wall can be obtained⁹⁾. With a slit one can also make observations in the 1-2 plane. However, for reasons which will be discussed later, it does not appear possible to make good measurements in this plane.

The present instrument, built for transparent, but also merely translucent materials, such as rubber-modified polystyrene, is of a rugged construction. It was developed from slit viscometers used in flow visualisation studies¹⁰⁾. In this study slits of differing dimensions were used. They were all built according to the same principle of construction. A schematic drawing of one such slit is given in Fig. 2.7.

Fig. 2.7 Schematic drawing of essential components of apparatus: H_1 , H_2 , and H_3 - heating bands; V - conical inner section containing slit; A - outer body; W - windows and holder for 1-3 plane measurements; E - entrance to slit.

Fig. 2.8 Geometry of flow through the slit: 1, 2 and 3 indicate coordinate system: 1 is flow direction; 2 is the direction of changing shear gradient. AA' for 1-2 plane measurements; BB' for 1-3 plane measurements.

The essential component of the apparatus is a conical member V which fits into a correspondingly machined outer body A. Part V has been split and a slit channel has been machined into it. The width of the channel is here 10 mm and the depth 1 mm. Fitted into the system are a set of glass windows of which two are clearly indicated (W in Fig. 2.7). These windows are situated 35 mm from the entrance of the slit and viewing through them corresponds to viewing along direction BB' in Fig. 2.8. The other four windows correspond with direction AA' in Fig. 2.8. Two of the latter windows are near the entrance, E, of the slit and the other two are situated at the same level as W. The windows fit sufficiently well to avoid perturbation of the flow (they may protrude into the channel by at most 0.02 mm). The temperature of the whole is determined by three independently controlled heating bands H_1 , H_2 and H_3 . The apparatus can either be mounted on a screw extruder for high shear rates (up to 10^3 s^{-1}) or onto a ram extruder for low shear rates (0.5 to 15 s^{-1}).

If the slit is of a sufficiently large cross-section ratio (width/depth ≥ 10) the flow gradient will change sharply only in the 2-direction, and it will be constant over the major portion of the 3-direction of the slit. With plane polarized light in direction AA' any measured birefringence will correspond to the 1-2 plane (Fig. 2.8) and vary with the position of the microscope with respect to the 2-direction. Near the walls of the slit the birefringence will be maximum and in the centre it will be zero. That means that one is not able to obtain measurements near the centre, where one would expect the highest accuracy from the point of view of undisturbed light propagation. Birefringence measurements taken in the direction BB', correspond to the 1-3 plane and the optical effect gives $n_{11} - n_{33}$. However, in the direction BB' the path difference is the sum over an inhomogeneous stress field since the shear stress is zero in the centre plane of the slit and maximum at the walls (see Section 2.5). The optical result then corresponds to an average value over the whole stress field. Actually measured by the compensator is the path difference P. If one takes a shear layer, dy, at a distance from the centre plane of the slit, then its contribution to the total path difference will be:

$$dP = (n_{11} - n_{33})dy \quad (2.2.1)$$

The total path difference will be:

$$P = 2 \int_0^{a/2} (n_{11} - n_{33}) dy \quad (2.2.2)$$

where, a, is the depth of the slit in the direction BB'.

This is an equation of the type which will also be met in the section on slit viscometry. It is based on the assumption of symmetry with respect to the central plane. To obtain the solution, the assumption is made that the shear stress, τ , varies linearly in the direction BB'. This is always true when the pressure distribution along the slit is linear and a very good approximation when the pressure distribution is non-linear (corrections of the order $a^3 d^3P/dx^3$ need to be added). Equation (2.2.2) then becomes on using the proportionality of the shear stress to y:

$$P = \frac{a}{\tau_w} \int_0^{\tau_w} (n_{11} - n_{33}) d\tau \quad (2.2.3)$$

where τ_w is the shear stress at the wall. The average birefringence is simply P/a . If this is termed, ϕ , then the solution of the above equation, as obtained by a rearrangement and differentiation with respect to τ_w , is:

$$(n_{11} - n_{33})_w = \phi \left(1 + \frac{d \ln \phi}{d \ln \tau_w} \right) \quad (2.2.4)$$

where the subscript, w , indicates that the quantities concerned are to be taken at the wall of the die. Quantity ϕ is measured as a function of τ_w and the relation (2.2.4) allows one to calculate $(n_{11} - n_{33})_w$ as a function of τ_w .^{*} The restrictions on the validity of this relation are not so severe as in the case of the corresponding Rabinowitsch equation for the velocity gradient (see Section 2.5). In steady flow, at a given stress level, the birefringence is either independent of the temperature or only a weak function of it. Also it is probable that pressure can only exert a very weak effect although there have been no experiments to confirm this. However, the above result, i.e. (2.2.4) is only of general validity at sufficiently large distances downstream so that the entrance stresses due to longitudinal gradients have died away.

More than one slit was used in this investigation. The essential dimensions of all the slits which were used, are given in the Table 2.1.

Table 2.1

slit	length (l) (mm)	depth (a) (mm)	breadth (b) (mm)	l/a
A	50	1	10	35;15
B	50	1	30	35;15
C	50	2.5	30	15;6
C1	58	1	20	60
C2	58	0.6	2	96
D	50	1	10	35

The slit C was large enough for slits C1 and C2 to be inserted into its channel. All slits, except slit D, had flat entrances. Slit D has a gradual opening at its entrance as it was built to avoid dead corners with PVC extrusion. The object in using so many slits was to check the influence of the slit aspect ratio on the optical performance and secondly to examine the influence of the channel length on the orientation.

*Later in the text the symbol $\langle n_{11} - n_{33} \rangle$ is sometimes used instead of ϕ .

Measurements in the 1-2 plane

The slit device can also be used for measuring the birefringence $\Delta n (= n_I - n_{II})$ in the 1-2 plane, where the principal values n_I and n_{II} should not be confused with the components n_{11} and n_{22} which are related to the corresponding normal stresses p_{11} and p_{22} . (Cf. Eqs (1.3.3), 1.3.6) and (1.4.2)). Measurement takes place in the direction AA' (Fig. 2.8). In view of the linear stress field which should be seen in the ocular, one expects zero optical effect in the centre of the field and an increasing optical effect on both sides of a central dark line. In white light this means coloured bands on either side of a symmetrically placed black line. In addition, one expects an extra black band parallel to the central band (line) but positioned according to extinction angle, χ : at an arbitrary orientation of the crossed polarizers somewhere on one side of the central line, the main directions of the refractive index ellipsoid will coincide with the directions of the polarizers. On rotation of the polarizers, a dark line should shift over the whole field. However, it turns out to be very difficult to make effective measurements in this plane. The first difficulty, which arises from alignment, is here more important than in other devices, owing to the non-homogeneous structure of the flow field. A good alignment is obtained by illuminating the slit with convergent light and adjusting the slit until the outcoming reflections from the two walls are symmetrically placed. The finer adjustment by which the image in the microscope is made perfectly symmetrical, then follows. It now turns out that with polymer melts and white light, there is no central black fringe except when the analyzer-polarizer combination is orientated in the stream direction or when the outputs are relatively low. The cause of this effect, which was not originally foreseen, is a parasitic shear flow (q_{13}) against the viewing windows. More serious is the absence of a clear fringe which should represent the extinction angle. The best that can be seen with polyethylene and polystyrene melts is a shadow covering one half of the image. The reasons for this failure are still not fully clear. There appear to be two main causes, both of which can give rise to the mixing of phase differences. As a consequence of these effects the extinction angle becomes indistinct.

A) Wall effects : Owing to the absence of slip, the orientation of the material is determined by a parasitic shear stress on the window as well as by the main shear stress on the larger wall. As a result, the light beam passes through regions of different orientation. This leads to errors of the kind mentioned at the end of 2.1.1. A further complication, possibly associated principally with the wall effect in as far as the birefringence is highest there, is the splitting of the light beam into ordinary and extraordinary beams. This manifestation has been seen with polyethylene melts where at very high shear stresses the emerging (and diverging) light beam contains differently polarized elements even when the ingoing light was unpolarized.

B) Friction heating : Friction heating always takes place. In equilibrium at some distance from the entrance to the conduit, the melt will be at a higher temperature in the centre than at the walls. The melt then acts as a lens diverging any passing light. The existence and importance of this effect could be

demonstrated by observations on a highly viscous PMMA. This material is optically isotropic at temperatures of about 150 °C. Extrusion of this material at this temperature was associated with a large lens effect; the temperature distribution could be measured with the help of the requisite Schlieren optics. It appears that even quite small temperature gradients are sufficient to cause serious mixing of light rays passing zones of varying birefringences.

Measurements in the 1-2 plane may nevertheless become necessary in order to estimate the stress optical coefficient required for further interpretation of the 1-3 plane measurements with a slit. For example, some materials, such as rigid PVC are unsuitable for measurement with the cone-and-plate apparatus at elevated temperatures (circa 200 °C). The stress optical coefficient then has to be estimated from the 1-2 plane results of the slit via the relation:

$$\Delta n \sin 2\chi = 2Cp_{12} \quad (2.2.5)$$

One uses monochromatic light. The analyzer and polarizer are crossed and set parallel and perpendicular to the flow direction. The distribution of fringes is measured in a microscope. Each fringe corresponds to a path difference $m\lambda$ ($m = 0, 1, 2, \dots$), where λ is the wave length of the light concerned. The measurements at one output then lead to the relation between the shear stress and Δn . Measurements can also be made at a second output as a check. It appears that the procedure always is accompanied by a large amount of scatter. The polystyrenes and the polyethylenes are not measurable at very high shear stresses owing to the lens effect arising from A or B. The value found for Δn from each fringe is set out against the shear stress calculated for the location of the fringe, on the assumption that the shear stress increased linearly from the central plane to the wall. The shear stress at the wall is found by slit-viscometry (see Ch. 2.5). The initial slope of Δn vs shear stress (linear paper) is evaluated to obtain the stress optical coefficient C ($\sin 2\chi = 1$ in the limit of zero shear stress). A few examples of this method will be shown in Chapter 5.

In one recent publication, other authors obtained, with a slit apparatus very similar to the one described, successful optical measurements, including the extinction angle, in the 1-2 plane¹¹⁾. We point out here, however, that they only showed results for the low stress region, i.e. less than 10^4 N/m². The present attempts were more aimed at the high stress region, i.e. 10^5 N/m² and higher, as the low stress region was covered by the cone-and-plate apparatus.

2.3 The Capillary Apparatus : Measurements in the 2-3 Plane

Freundlich¹²⁾ shew the existence of non-zero $n_{22} - n_{33}$ for V_2O_5 sols by viewing along the axis of a short capillary. Later, Philippoff made the first serious attempts to quantify and classify different materials by this method¹³⁾. With the help of a capillary and, at a later date, with the help of a slit, by viewing along the axis between crossed nicols, he tried to measure the optical effect ascribable to $n_{33} - n_{22}$. With the polymeric materials he examined, which were in the freely flexible state, he was unable to detect an effect and there-

fore concluded that for these systems $n_{22} - n_{33}$ must be zero. The solutions that he examined were highly elastic; melts of high viscosity were not examined. He could show, as is expected theoretically, that suspensions of rigid particles (also certain polymer solutions with suitable solvent) gave a very strong effect corresponding to a non-zero $n_{22} - n_{33}$. For the examination of molten polymers, this author built a sturdy device based on the apparatus of Philippoff. Figure 2.9 is a diagrammatic representation of the main features

Fig. 2.9 Diagrammatic representation of the main features of the apparatus.
E (cylinder); H (heating bands); W₁ and W₂ (windows); I (capillary);
C (compensator); P (polarizer); A (analyzer); M (microscope).

of the apparatus. The body of the apparatus is formed by a hollow cylinder of nitrided steel E, inner diameter 15 mm, outer diameter 75 mm. At the lower end the cylinder E has been drilled to make room for a window W₁ and for the capillary I. The capillary projects out of the cylinder. The inner diameter of the capillaries was usually 2.67 mm and the inner surface was honed. Three capillaries of length 40 mm, 20 mm and 7 mm were used. Heating elements H completely surround all parts. Temperature can be controlled to within 1 °C at four places

in the system (one in the capillary and three in block E). The light path is schematically given in this figure; light passes through a polarizing sheet P, then through a first window W_1 , axially along the capillary, through a second window W_2 . Finally it passes through a compensator C and analyzing polaroid, and into the observer's microscope M.

The reservoir R is first filled either with granulate or with melt. The necessary time is allowed for thermal equilibrium and the piston which is controlled by a variable speed motor, is set in motion. In the viewer's microscope (Fig. 2.9 under) a typical Maltese cross is seen on flow, with the microscope focussed in the capillary. During compensation (the compensator is set at 45° to the crossed polarized sheets) the cross splits into two fringes which move towards the edge formed by the wall of the capillary. Compensation is achieved when the apex of each fringe is judged to be at the wall of the die. In general the view in the microscope is fairly symmetric, considering the amount of gel particles and dust always present in commercial melts, and the fact that the downward exit from the chamber before W_2 had to be placed asymmetrically. Measurements could not ordinarily be carried out at gradients which would lead to birefringences much greater than 10^{-5} , as extinction with the compensator became progressively difficult. This, we must assume, is the result of depolarization caused by:

- 1) the bending over of the flow lines near the entrance and the exit;
- 2) a mixing effect due to frictional heating;
- 3) a mixing effect caused by beam splitting due to the birefringence.

The last effect is perceptible in any birefringent medium of sufficient working thickness, when the light beam does not coincide with a principle optic axis.

The shear stress was not obtained directly with the apparatus. Instead, the measured path differences were correlated to the reduced output D_c .

$$D_c = \frac{4 Q}{\pi R^3} \quad (2.3.1)$$

where Q is the volume output per unit of time and R is the radius of the capillary.

Each material investigated had to be calibrated so that a correction (the so-called Rabinowitsch correction) could be applied to obtain the gradient at the walls of the die from the D_c values¹⁴). In order to examine the influence of the entrance and the exit disturbances, the optical effects were measured with a set of capillaries of varying length and set out against the length of the capillary.

2.4 Measurement of the Path Difference

There are many methods, a full description of all of them is beyond the scope of the present work. In the simplest case the phase difference between two plane polarized rays of monochromatic light vibrating in perpendicular planes amounts to an integral multiple of 2π , say, $2\pi m$. The emergent light is then extinguished by the analyzer. The birefringence is then given by:

$$\Delta n = m \frac{\lambda}{d} \quad (2.4.1)$$

where λ is the wavelength of the light concerned, and d the thickness of the working section. In liquids, m can be found for monochromatic light by steadily increasing the shear stress and counting the extinctions as they pass by: the first gives $m = 1$, the second $m = 2$, etc.

Under normal circumstances, one requires measurements of path differences which are fractions of the wavelength being used. In the present work, this was achieved chiefly by the use of the Ehringhaus compensator¹⁵⁾, well-known to the users of polarizing microscopes. The principal of this compensator lies in the use of a rotating combination of two crystals of quartz or calcite. The combination is placed in the path of the light ray immediately after the double refracting material to be measured. The crystals have been cut and combined, so that no phase difference is present when the combination is in an exactly perpendicular position with respect to the light beam. On rotation about a principal axis perpendicular to the light path, a birefringence effect is produced. By placing the axis of rotation of the instrument successively in two mutually perpendicular positions, the subtraction position can be found and, in this way, the sign of the birefringence effect can be determined. In use the apparatus is simple: it is set so that the axis of rotation of the crystal coincides with one of the extinction directions of the material to be measured. The crystal is rotated, producing a phase shift, which either adds to or subtracts from the phase shift produced by the material. With monochromatic light extinction is then obtained when the sum of the path differences is an integral multiple of 2π . In normal use the subtraction position is used and the method is one of compensation. The relation between the crystal rotation, read from a scaled drum, and the phase shift, is supplied in a manual of the manufacturer (Carl Zeiss, Oberkochen, Württ.). The tables were spot checked and found to be very accurate. Compensation carried out in this way always gives the phase difference apart from some multiple of 2π . The multiple is not directly obtainable in monochromatic light, but is usually evident if one, for instance, works with steadily increasing stresses. It can also be determined by using white light as extinction only occurs in this case, when the phase shift produced by the crystals is equal but opposite in sign to that of the material.

2.5 The Slit Viscometer

Viscosities can be determined with dies of rectangular cross-section. When the ratio of the longer side to the shorter side, i.e. the aspect ratio, is sufficiently great, the system approximates to two parallel plates. The advantage of slit viscometry over the more common capillary viscometry using capillaries of circular cross-section, is that the measurement of the pressure gradient in the flow direction is easily made at the wall of the die. An essential requirement for such measurements is that the pressure device does not influence the flow. For this reason measurements of the pressures are made with electronic pressure gauges¹⁶⁾, for which the transducer displacement is very small, relative to the dimensions of the slit channel.

For Newtonian fluids the influence of the edge effects in infinitely long ducts is known exactly for all aspect ratios of the slit - at least in the slow flow region. Experimental investigations have verified the solutions for slits of aspect ratios less than ten¹⁷⁾. In a previous investigation¹⁸⁾ with

polyethylene melts, it was found that there were no measurable, systematic, differences between dies of aspect ratios 10 : 1, 20 : 1, and 30 : 1.

The assumption is now made that, for experimental purposes, an aspect ratio of 10 : 1 or greater is sufficient to achieve a reasonable approximation to fluid behaviour between two infinite parallel planes.

The physically measured quantity is the distribution of the normal pressure, P_{22} , along the wall of the slit channel. When the distribution is linear, the shear stress at the wall of the die is given by the slope of the pressure distribution.

$$P_{21,w} = \tau_w = - \frac{b}{2} \frac{dP_{22}}{dx} \quad (2.5.1)$$

where b is the depth of the slit and x is the distance of a pressure gauge from the slit entrance. Often a linear pressure distribution along the die is not obtained. In this case equation (2.5.1) gives the local shear stress at the wall of the die to within a very good approximation. The full expression contains higher derivatives as well, but these lead to corrections of the order of 0.01 % only. The normal pressure, P_{22} , consists of a hydrostatic component and a deviatoric component. The deviatoric component for the usual conditions of flow rate, temperature, etc., is estimated to be of the order of a few bars at most and, probably nearly constant along the slit. Its precise value is determined by the stress conditions at the die exit. Under the conditions of this work, P_{22} , can be equated to the hydrostatic pressure.

To obtain the viscosity, having obtained the shear stress at the wall, one needs the velocity gradient at the wall. This is obtained from a version of the Rabinowitsch correction already known for capillary flow¹⁴). The volumetric output, Q , per unit of time is to the usual approximation given by:

$$Q = 2 b \int_0^{a/2} V(y) dy \quad (2.5.2)$$

where b is the breadth of the slit and $V(y)$ the velocity at a distance y from the plane of flow symmetry (conditions of laminar flow). The first assumption needed for the present purpose is, that slip does not occur at the die wall. Partial integration then leads to:

$$Q = 2 b \int_0^{a/2} y \frac{dV}{dy} dy \quad (2.5.3)$$

The absence of slip condition has been experimentally confirmed for unfilled polymers under normal processing conditions by direct observation on several systems^{10,19}). The variable under the integral may be transformed by using the already mentioned linear relation between the shear stress and the distance y of a shear plane from the central plane. In this way one finds:

$$\frac{6 Q}{b a^2} = D_s = \frac{3}{\tau_w^2} \int_0^{\tau_w} \tau q d\tau \quad (2.5.4)$$

where q ($= dV/dy$) is the shear gradient and τ is the shear stress at y . Quantity D_s is called the reduced output. By introducing the factor 6 on both sides of the equation, D_s has become the shear rate at the wall, if the investigated fluid is Newtonian. The solution to (2.5.4) is found by rearrangement and by differentiation with respect to τ_w . There is obtained:

$$q_w = D_s \left[\frac{2}{3} + \frac{1}{3} \frac{d \ln D_s}{d \ln \tau_w} \right] \quad (2.5.5)$$

There are two restrictions to the above relation. The flow should be isothermal and the viscosity should not depend on the hydrostatic pressure. The isothermal condition means that not only should the melt entering the duct be at the correct temperature, but also shear heating should be absent. The pressure condition can be relaxed by evaluating the shear stress at a constant pressure level, i.e. at places along the slit which depend on the reduced output D_s . Usually, the shear stress is evaluated at the exit of the slit, corresponding to zero hydrostatic pressure. When the above conditions are fulfilled the relation between the shear gradient at the wall and the reduced output becomes:

$$q_w = D_s \left(\frac{2 + n}{3} \right) \quad (2.5.6)$$

where $n = d \log D_s / d \log \tau_w$ is simply the slope on a log-log plot of the experimental relation between D_s and τ_w . This relation in combination with the shear stress at the wall allows one to determine the viscosity as function of the shear gradient. The corresponding relation for circular capillaries reads¹⁴⁾:

$$q_w = D_c \left(\frac{3 + n}{4} \right) \quad (2.5.7)$$

where D_c is given by (2.3.1) and $n = d \log D_c / d \log \tau_w$ for this case.

A slight peculiarity of the slit (or capillary) viscometer method becomes apparent: one obtains properties of the material at an interface. One cannot be completely sure that this is not somehow different from the properties of the bulk material.

Since, however, the boundary surfaces are not smooth on a molecular scale, the foregone results for finding the stress and the gradient at the wall must allude to an average boundary formed in part by the container walls and in part by the bulk material. If, in fact, the interface was important, then changes in the container, in material, in surface smoothness, should produce noticeable effects. Whilst such effects have been reported from time to time²⁰⁾ there does not seem to be any reason that for normal, unfilled, polymer melts of this investigation a wall effect might be present (cf. Ref. 10).

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3. Materials

Most measurements described in this work were performed on melts of polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), polydimethylsiloxane (PDMS), polypropylene (PP), and polyvinylchloride (PVC). The following table gives the specific materials used, the experiments carried out, and the temperature of measurement.

Table 3.I

polymer	name	temperature(s)	measurements
PS	Styron 666	140-200	1,2,3,5,6
	Styron 678	140-190	1,3,4,5,6
	Styron 475	140-190	3
	BASF 3	150-220	1,3,4,6
	S111	190	1,3,5,6
	PC 3a	200	1,3,5
	PC 4a	168	1
	PC 5a	200	1
	PC 6a	214	1,3,5
	PC 7a	158	1,3,5
	PC 14a	242	1
LDPE	Alkathene 2	190	3
	LDND	150	1,5
	LDDB	150	1,5
	IUPAC A	150,190	1,3,4,5
HDPE	HDND	150	1,5
	HDBD	150	1,5
	Marlex 6050	190	1,3,4,5,6
PDMS	Siloprene RS	22	1,4,5,6
	E 302	22,105,190	1
PP	PPND	210	1,5
	PPBD	210	1,5
PVC	Solvic 229	180-210	2

The measurements performed were:

- 1 = Δn and χ in the 1-2 plane with the cone-and-plate apparatus
- 2 = Δn in the 1-2 plane with the slit apparatus
- 3 = $(n_{11} - n_{33})$ of the 1-3 plane with the slit apparatus
- 4 = $(n_{22} - n_{33})$ of the 2-3 plane with the capillary apparatus
- 5 = viscosity with either capillary, slit or cone-and-plate apparatus
- 6 = dynamic shear moduli $G'(\omega)$ and $G''(\omega)$

Styron 666, 678 and 475 are general purpose and injection moulding grades of polystyrene produced by the Dow Chemical Corporation, Midland, Michigan, U.S.A. The same company kindly supplied the narrow molecular weight distribution polystyrene S111. PC 3a to 14a are polystyrenes of narrow molecular weight distribution supplied by the Pressure Chemical Company of Pittsburgh, Pennsylvania, U.S.A. BASF 3 was obtained from the BASF, Ludwigshafen, Germany.

The polyethylenes were obtained from I.C.I., Welwyn Garden City, England (Alkathene 2); Monsanto Chemicals Limited, Newport, Monmouth, England (LDND and LDBD)*; BASF (IUPAC A); and Dow Chemicals (HDBD and HDND). The last mentioned polymers have been the subject of IUPAC Working Party investigations³⁾⁷⁾.

The polypropylenes were from the Shell Plastics Laboratory, Delft, Holland (PPND and PPBD).

The polydimethylsiloxanes were commercial polymers supplied by Bayer, Leverkusen (Siloprene RS) and by Midland Silicones (E 302).

The polyvinylchloride, Solvic 229, was supplied by Solvay & Cie, Brussels, Belgium.

Molecular Weights

One of the aims of this investigation is to study the relation between the molecular weight and its distribution on the rheological properties. A full and complete knowledge of the molecular weight distribution is not possible. The nearest approximation that exists is a Gel Permeation Chromatogram (GPC). However, the details of the high molecular weight tail, so important for the rheological properties, is often obscured and the interpretation of GPC curves is still a matter for investigation. In practice only two molecular weight averages are regularly determined: M_n the number average molecular weight, and M_w the weight average molecular weight. Even these quantities are difficult to obtain with confidence to within 10 % and literature values for commercial polymers can show disparities as great as 50 %. [In the table 3.2. examples of such great disparities are to be found.] The higher averages M_z and M_{z+1} can be determined either from sedimentation equilibrium experiments (ultracentrifuge) or from an analysis of the GPC curves. The accuracy of these latter methods for the higher averages is less than that for the number and weight average molecular weights. The data available on the measured polymers is given in the following table, together with the source.

*LD = low density; HD = high density; ND = narrow, BD = broad distribution of molecular weights.

Table 3.2

material	molecular weights in 100,000				source
	M_n	M_w	M_z	M_{z+1}	
1a	1.54	1.6	-	-	1
	2.54	1.63	1.76	(2.26)	2
3a	3.92	3.93	-	-	1
	4.02	3.93	4.21	-	2
4a	0.98	0.96	-	-	1
	-	0.94	0.98	-	2
5a	4.04	5.07	-	-	1
	4.35	5.20	5.93	(6.77)	2
6a	7.35	8.62	-	-	1
	-	7.90	8.30	-	2
7a	0.49	0.51	0.54	-	2
14a	16.1	17.0	-	-	1
	-	14.2	15.8	-	2
S111	2.14	2.24	-	-	3
Styron 666	1.08	2.71	6.0	12.0	4
	0.92	2.3	-	-	5
	1.66	3.66	-	-	6
Styron 678	0.90	2.40	5.3	11.0	4
BASF 3	0.82	4.1	12.5	18.0	2
HDND	0.11	0.44	-	-	3
HDBD	0.11	1.6	12	-	3
LDND	0.2	1.0	3.0	-	3
LDBD	0.15	2.5	24	-	3
IUPAC A	1.17	5.4	-	-	7
Marlex 6050	0.1	0.84	-	-	8
	0.12	1.53	9	-	9
Solvic 229	0.67	1.4	2.5	3.7	4

Literature

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4. Theories

4.1 Molecular Theories

Molecular theories of the hydrodynamic behaviour of polymeric systems began to appear some thirty years ago with the work of Kuhn¹⁾. At that time particular interest was paid to dilute solutions. The first requirements of any molecular theory are expressions for the refractive index and the stress tensors. For relations with these quantities only some special features are identical. and melts, the same or similar expressions may be used for the contribution of each molecular chain to the total macroscopic effect. Sometimes a whole molecule is considered as a "chain", sometimes only a segment of a molecule, e.g. between two "entanglements". The final macroscopic effect is to be obtained by the simple sum over all the chains present.

The Stress Tensor

The contribution, Δp_{ij} , of a single chain to the macroscopic stress, p_{ij} , is given by:

$$\Delta p_{ij} = - \langle x_i F_j \rangle \quad (4.1.1)$$

where x_i is the x_i ($i = 1, 2, 3$) coordinate of one chain end with respect to an origin of coordinates at the other end and is, therefore, essentially the probability that the chain crosses a unit area on the j, k plane; F_j is the x_j component of the statistical force exerted between the chain ends and $\langle \rangle$ signifies that the whole needs to be averaged by the distribution function of the chain ends. The above expression has been derived in a simple way by Hermans²⁾ and more rigorously by Kramers³⁾. Similar expressions have also been given by Kirkwood and Riseman⁴⁾ (using the Oseen expression for the perturbation of the solvent velocity field); Fixman⁵⁾, and others⁶⁻⁹⁾ who studied the application of the time correlation method to polymer chain dynamics.

To (4.1.1) there should be added a term due to the momentum transfer between the particles. This correction is important for low molecular weight liquids, but along with other corrections is considered negligible for polymeric solutions and melts in the normal range of shear rates. The macroscopic stress p_{ij} is obtained by summing over all the molecular chains, m , present and reads:

$$p_{ij} = - \sum_m \frac{N_a c_m}{M_m} \langle x_i F_j \rangle_m \quad (4.1.2)$$

where N_a is Avogadro's number and c_m the concentration of the chains of molecular weight M_m . The simple addition of the supposed average contribution of each molecule to form the total macroscopic stress is one of the basic hypothesis of these molecular theories. The traditional model thus assumes all interactions can be smoothed out in order to form the average medium in which each molecule is free to react to the forces acting upon it.

The Refractive Index Tensor

Refraction is described by a refractive index n related to the polarization, β_m , per molecule formed by the chain elements in vacuum and the reaction field from the surrounding elements.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi \sum_m \beta_m \frac{N_a c_m}{M_m} \quad (4.1.3)$$

where again N_a is Avogadro's number, c_m the concentration, and M_m the molecular weight of the species m . The above is the Lorentz-Lorenz relation which is only strictly valid if the molecular dipoles are in structures of cubic or tetrahedral symmetry¹⁰). For the anisotropic state the above relation is assumed valid when corresponding components of the refractive index and polarizability tensors replace n and $\beta_m^{(11)}$. This leads to:

$$\left[\frac{n^2 - 1}{n^2 + 2} - \frac{6n^2}{(n^2 + 2)^2} \right] \delta_{ij} + \frac{6n}{(n^2 + 2)^2} n_{ij} = \frac{4}{3} \pi \sum_m \beta_{ij} \frac{N_a c_m}{M_m} \quad (4.1.4)$$

where n is now the average refractive index given by $3n = n_{11} + n_{22} + n_{33}$.

The quantities which are obtainable from birefringence experiments are $n_{11} - n_{22}$, $n_{11} - n_{33}$, $n_{22} - n_{33}$ and n_{12} . We are not interested in the isotropic term factoring δ_{ij} .

For the measurable quantities there is obtained:

$$n_{ii} - n_{jj} = \frac{2}{9} \frac{\pi (n^2 + 2)^2}{n} \sum_m \frac{N_a c_m}{M_m} (\beta_{ii} - \beta_{jj})_m \quad (4.1.5)$$

There is now needed an expression for $\beta_{ii} - \beta_{jj}$, the anisotropy of the molecule. We follow the path originally taken by Kuhn and Gr $\ddot{u}$ n¹²), and smooth out the real optical structure of the chain by using average random link quantities. The assumption is made that the polarizabilities of the random links are additive and independent of the various chain conformations. Both assumptions are disputable; the reaction field round a dipole is a function of the neighbours of the dipole and their orientation.

The process of averaging out the bond polarizabilities into polarizabilities of random links takes the first point, at least partially, into account. In doing this we lose, however, the possibility of interpreting the results quantitatively in terms of the molecular structure of the chains. The second point implies that the Lorentz-Lorenz field will not be correct when the material is seriously orientated. This point will be discussed later.

To each of the N random links, which constitute the chain, is assigned a polarizability α_1 in the axial direction and a polarizability α_2 perpendicular to this direction. Kuhn and Gr $\ddot{u}$ n showed that as long as one can neglect saturation effects (which is the case for deformations small compared with the chain contour length), the mean optical anisotropy of a chain, $\Delta\gamma$, after averaging over all possible conformations at fixed end-to-end distance r , is given by:

$$\Delta\gamma = \frac{3}{5} (\alpha_1 - \alpha_2) \frac{r^2}{r_0^2} \quad (4.1.6)$$

where $(\alpha_1 - \alpha_2)$ is the optical anisotropy of the random link; r_0^2 the mean square of the end-to-end distance of the chain in undeformed state. The components of the chain polarizability, β_{ij} , in the laboratory frame of reference are given by:

$$\beta_{ij} = \langle \gamma_2 \rangle \delta_{ij} + \langle (\gamma_1 - \gamma_2) \cos \theta_i \cos \theta_j \rangle \quad (4.1.7)$$

where θ_i is the angle between the chain end-to-end vector and the i coordinate axis; $(\gamma_1 - \gamma_2) = \Delta\gamma$. Also $\langle \gamma_2 \rangle$ is a function of the chain stretching and is given by:

$$\langle \gamma_2 \rangle = N \left(\frac{\alpha_1 + 2\alpha_2}{3} \right) - \frac{1}{5} (\alpha_1 - \alpha_2) \frac{\langle r^2 \rangle}{r_0^2} \quad (4.1.8)$$

where N is the number of random links. If one end of the chain is held at the origin of coordinates and the other at (x_1, x_2, x_3) , $\cos \theta_i$ reads:

$$\cos \theta_i = \frac{x_i}{r} \quad (4.1.9)$$

By substituting (4.1.6) with (4.1.9) in (4.1.7) there is obtained for β_{ij} :

$$\beta_{ij} = \langle \gamma_2 \rangle \delta_{ij} + \frac{3}{5} (\alpha_1 - \alpha_2) \frac{\langle x_i x_j \rangle}{r_0^2} \quad (4.1.10)$$

and for the birefringence:

$$n_{ii} - n_{jj} = \frac{6\pi}{45} \frac{(n^2 + 2)^2}{n} (\alpha_1 - \alpha_2) \Sigma \frac{N a c_m}{M_m} \frac{\langle x_i^2 - x_j^2 \rangle_m}{r_0^2} \quad (4.1.11)$$

The extinction angle, χ , for shear flow in the 1-2 plane follows:

$$\cot 2\chi = \frac{n_{11} - n_{22}}{2 n_{12}} = \frac{\langle x_1^2 - x_2^2 \rangle}{2 \langle x_1 x_2 \rangle} \quad (4.1.12)$$

The Stress-Optical Relation

Let us remark that if the linear expression from rubber elasticity for the force between the chain ends is applied, we automatically obtain the stress-optical relations 1.4.1. and 1.4.2.

The force between the chain ends is¹¹⁾:

$$\underline{F} = - 2\mu kT \underline{r} \quad (4.1.13)$$

where μ is a function of the mean square end-to-end distance in equilibrium.

$$\mu = 3/2r_0^2 \quad (4.1.14)$$

When this expression is combined with (4.1.2) it is immediately found that the orientations of the stress tensor and the optic tensor coincide and that the deviatoric components are related by linear relations¹³⁾.

$$n_{11} - n_{22} = C(p_{11} - p_{22}) \quad (4.1.15)$$

$$n_{11} - n_{33} = C(p_{11} - p_{33}) \quad (4.1.16)$$

$$n_{12} = C p_{12} \quad (4.1.17)$$

where C is a deformation independent parameter, i.e. the stress optical coefficient given by:

$$C = \frac{2 \pi}{45 kT} \frac{(n^2 + 2)^2}{n} (\alpha_1 - \alpha_2) \quad (4.1.18)$$

4.2 The Distribution Function (Basic Theory)

The averages $\langle F_i x_j \rangle$ and $\langle x_i x_j \rangle$ needed for the stress and refractive index tensors, have to be supplied by a distribution function. In the course of this chapter it will be seen that it is often only necessary to obtain the differential equation governing the distribution function and not have to solve it explicitly. The basic procedure is to obtain a Smoluchowski equation for chains. In one of the original treatments, Kirkwood¹⁴⁾ formulated the equation in terms of a real chain space. Kirkwood hoped to relate the hydrodynamic behaviour of the real chain to the hydrodynamic resistances of its individual atomic groups. This is now thought to have been too optimistic and consequently one replaces the atomic structure by a model structure. The real chain is hereby replaced by a row of N point resistances - "beads" - connected by springs, subject to ordinary hydrodynamic friction. The points are sufficiently far apart that their actions are uncorrelated; a complete description of all their movements therefore requires a $3N$ -dimensional space.

One begins by writing down the equation for the conservation of mass. In terms of the distribution function ψ which represents the probability function for the density of the segments; this has the form:

$$\frac{\partial \psi}{\partial t} + \text{Div}(\psi \phi) = 0 \quad (4.2.1)$$

where ϕ is the flux of segments in $3N$ -dimensional configurational space.

We now need expressions for this flux. In doing this, we shall follow the path usually taken by polymer scientists. There are two sources of flux: ϕ_1 and ϕ_2 . The first, ϕ_1 , is simply the macroscopic flow, $\underline{V}$.

$$\phi_1 = \underline{V} \quad (4.2.2)$$

The second, ϕ_2 , is formed by the forces on the chain. Magnetic, electrical and acceleration forces involving the masses of the beads are neglected. The further assumption is made that a force $\underline{F}$ will give a flux $\underline{D} \cdot \underline{F} / kT$ where the components of the (symmetric) tensor $\underline{D}$ are diffusion constants of individual beads, to be defined later. The two forces acting are:

a) *Brownian motion*: According to Zimm¹⁶⁾, the theories of Brownian motion^{17,18)} show that a bead acts as if it were subject to a force $-kT \text{ grad } (\ln \psi)$. This relation is not explicitly given by quoted references. From their results it can be shown nevertheless, that this should be a suitable relation provided the deviations from equilibrium are small.

b) *Restoring force*: To prevent the beads diffusing apart, a restoring force $\underline{F}$ must be present. In the absence of the macroscopic flow, $\underline{V}$, this force will be in equilibrium with the Brownian motion force, a). At present $\underline{F}$ is not stipulated, it may be a non-linear function of the state variables.

Equation (4.2.1) becomes on substituting the sources of flux, the diffusion equation in 3N-dimensional vector space.

$$\frac{\partial \psi}{\partial t} + \text{Div} [\underline{V} \psi + \underline{F} \cdot \underline{D} \frac{\psi}{kT} - \underline{D} \cdot \text{grad } \psi] = 0 \quad (4.2.3)$$

Equation (4.2.3) is a version of the Smoluchowski equation of diffusion. Somewhat confusingly, it is also referred to often as the Fokker-Planck equation. When the linear relation (4.1.13) is used for $\underline{F}$ we have the diffusion equation in basic form, as seen in the theories of Kuhn¹⁾, Hermans²⁾, Rouse¹⁵⁾ and Zimm¹⁶⁾. For this case, we may put the equation in a form which emphasizes the linearity of the theory.

$$\frac{\partial \psi}{\partial t} + \text{Div} [\underline{V} \psi - \underline{D} \cdot (\text{grad } \psi - \text{grad } \psi_0)] = 0 \quad (4.2.4)$$

where ψ_0 is the distribution function in the undisturbed state. Indeed we could have obtained the result directly by appealing to the Onsager relations from irreversible thermodynamics.

$$\text{Flux} = L_{pq} F_q(\alpha_1 \dots \alpha_n) \quad (4.2.5)$$

where α_p ($p = 1 \dots n$) is the deviation of the p^{th} state variable from the value at thermal equilibrium, F_q is the thermodynamic force defined as the derivative of entropy ($kT \log \psi$) with respect to α_q , and L_{pq} are (symmetric) transport coefficients. The forces F_q are considered to be linear in the deviations α_p . When now the α_p are considered to be the state variables instead of the deviations of the state variables from equilibrium the flux due to the forces has just the form of the ϕ_2 term as given in (4.2.4).

In this work we are chiefly interested in steady flow for which $\frac{\partial \psi}{\partial t} = 0$ and (4.2.4) takes the explicit form when the suffixes are added for the N beads¹⁹⁾ in cartesian coordinates.

$$\sum_{p,q}^N \nabla_{Rp} \{ \delta_{pq} \nabla_q \psi + D_{pq} F_q \frac{\psi}{kT} - D_{pq} \nabla_{Rq} \psi \} = 0 \quad (4.2.6)$$

The symbol R indicates that further suffixes have to be added for the three space directions. The physical interpretation of D_{pq} is that it represents the diffusion constant of bead p as modified by bead q . In dilute solutions the need for this refinement can readily be seen as the flow at bead q will disturb the flow around bead p ; in the extreme case the solvent becomes entrapped in the coil.

For melts and concentrated solutions on the other hand, it is considered that the bead q has no influence on the bead p . The reason for this belief lies in the observation that the interpenetration of neighbouring coils ensures that the surroundings of a segment move on average with the macroscopic flow field since the surroundings are coils whose centres of gravity drift with the average flow field²⁰⁾. In the context of the last remark, it is possible that low molecular weight components in a polydisperse mixture might be entrained in the way described for very dilute solutions. An additional and more pragmatic reason for ignoring hydrodynamic interaction in melts is contained in the difficulty of handling; there does not seem to be any non-Newtonian equivalent to the Oseen tensor⁴⁾ which has been so useful in describing the interaction for dilute solutions.

Since in this work we are not directly concerned with dilute solutions, we will ignore the possibility that the diffusion constant is a function of the bead position along the chain and treat it as a constant tensor.

$$D_{pq} = D \delta_{pq} \quad (4.2.7)$$

The above indices refer to the bead number; D may still be an anisotropic function in space, however. Equation (4.2.6) then simplifies to the following equation when the summation over the space coordinates are explicitly included:

$$\sum_{i,j=1}^3 \sum_{p=1}^N \frac{\partial}{\partial x_i^p} [D_{ij} \frac{\partial \psi}{\partial x_j^p} - D_{ij} F_j^p \frac{\psi}{kT} - V_i^p \psi] = 0 \quad (4.2.8)$$

where i, j refer to the ordinary ($1 \equiv x, 2 \equiv y, 3 \equiv z$) space coordinates; x_i^p is the i -component (x, y , or z) of the p bead based on the space coordinates; D_{ij} are the components of the diffusion tensor; V_i^p is the i -component of the macroscopic flow at bead p , i.e. the macroscopic fluid velocity at that place. The diffusion coefficients D_{ij} are for polymers invariably chosen from the translational diffusion coefficients of the hydrodynamic centres of resistance (beads). The terms involving the rotation diffusion coefficients of the beads are neglected. In principle, each segment both rotates and translates. However,

with increasing distance from the hydrodynamic centre of the total molecule, the translational resistance dominates.

4.3 The Elastic Dumbbell Model

This model originated from the pens of Kuhn¹⁾ and Hermans²⁾. In recent times it has waned in relative importance against the Rouse¹⁵⁾, Bueche²¹⁾, Zimm¹⁶⁾ models and their modifications²²⁾. Nevertheless, the model has been found useful since features of more involved models can be explored in a tentative way.

The model represents the polymer chain by two spheres connected by an elastic spring. All the hydrodynamic forces on the chain segments are lumped together and assumed to act only on the end spheres. The elastic spring is a representation of the statistical forces acting to balance the hydrodynamic forces. In the original models hydrodynamic interaction between the spheres was neglected. For reasons previously given, this aspect is also neglected here.

The origin of the space coordinates is set on one of the spheres. The coordinate of the other sphere with respect to this origin of coordinates, is simply:

$$\underline{r} = (x_1, x_2, x_3) \quad (4.3.1)$$

The diffusion tensor is assumed to be spherically symmetric; $D_{ij} = D\delta_{ij}$. Further, the assumption is made that the force between the beads is given by the linear expression from rubber elasticity, i.e. relation (4.1.13). This expression for the force was obtained by considering the average force between the chain ends when they are held $\underline{r}$ apart. The same linear approximation is obtained for the average distance between the chain ends when they are subject to a given force. When the deformation becomes significant with respect to the chain contour length and higher order terms have to be included, this correlation does not hold²³⁾. Thus, the extension of (4.1.13) to include non-linear terms, gives rise to conceptual difficulties.

With steady shear flow given by a gradient q in the x_2 direction, we have:

$$\underline{v} = (qx_2, 0, 0) \quad (4.3.2.)$$

Equation (4.2.3) becomes:

$$\text{Div} [\underline{v}\psi - 2\mu D \underline{r}\psi - D \text{grad } \psi] = 0 \quad (4.3.3)$$

Following J.J. Hermans²⁾ we now multiply the above in turn by x_1x_2 , x_1^2 , x_2^2 , x_3^2 and integrate over all space. In doing this, the reasonable assumption is made that ψ decreases exponentially at large distances from the origin. It is then possible to derive the following averages needed for the stress and refractive index components: $\langle x_1x_2 \rangle$, $\langle x_1^2 \rangle$, $\langle x_2^2 \rangle$, $\langle x_3^2 \rangle$. The results are:

$$\langle x_1^2 \rangle = \langle x_2^2 \rangle + 2q^2\tau^2\langle x_2^2 \rangle \quad (4.3.4)$$

$$\langle x_2^2 \rangle = \langle x_3^2 \rangle = 1/2\mu = r_0^2/3 \quad (4.3.5)$$

$$\langle x_1x_2 \rangle = q\tau\langle x_2^2 \rangle \quad (4.3.6)$$

where $\tau = (4 \mu D)^{-1}$ is called the relaxation time of the system. The gradient dependency of the extinction angle for a monodisperse system is given by (4.1.12):

$$\cot 2\chi = q\tau \quad (4.3.7)$$

i.e. a relation of the type proposed by Nantonson (see Introduction). It is seen that: the mean square projections of the dumbbells length onto the x_2 and x_3 axes are unaltered by the flow; the shear component $\langle x_1x_2 \rangle$ is linearly proportional to the gradient q , and that the normal component $\langle x_1^2 \rangle$ is changed proportional to the square of the gradient. This model therefore predicts:

- 1) The stress-optical law: since the expression for the force in the chain has been taken from the linear approximation.
- 2) Newtonian viscosity: since $\langle x_1x_2 \rangle$ is proportional to q . The full expression for the shear stress in steady shear flow reads when the sum over all molecules is included (4.1.2):

$$P_{12} = q \sum_m \frac{RT c_m}{M_m} \tau_m \quad (4.3.10)$$

where $\tau_m = 1/4 \mu D = fM_m^2$. Here it has been assumed that the diffusion constant D is inversely proportional to the molecular weight and f is a material constant which is a function of the polymer type and its surroundings. Factor f is related to the friction constant of a single segment. The expression (4.3.10) can be rewritten:

$$P_{12} = qcRTfM_w \quad (4.3.11)$$

- 3) A normal stress difference $p_{11} - p_{22}$ proportional to the square of the gradient. In a similar way to the last paragraph we find:

$$P_{11} - P_{22} = 2q^2 \sum_m \frac{RTc_m}{M_m} \tau_m^2 \quad (4.3.12)$$

and

$$P_{11} - P_{22} = 2q^2cRTf^2M_{z+1}M_zM_w \quad (4.3.13)$$

- 4) A normal stress difference $p_{22} - p_{33}$ equal to zero.

$$P_{22} - P_{33} = 0 \quad (4.3.14)$$

The Dumbbell Extended

We would like to see under which conditions the simple dumbbell model would give a behaviour qualitatively more in keeping with the experimental reality. Specifically, we are interested in obtaining unequal normal stresses p_{22} and p_{33} in the second order region. We do not consider rigid dumbbells, as these have been extensively considered^{24,25}, and because the stress-optical relation is not valid for these systems. Instead, we investigate two modifications in a simple way:

A) The expression for the force is left undefined, and the diffusion constant is again isotropic. In this way, the possible effects of non-linear springs can be examined.

B) The rubber elasticity expression for the force is retained, but it is assumed that the diffusion tensor of a typical segment between the chain ends has cylindrical symmetry. The diffusion constant of the end bead is in turn assumed to have a symmetry, determined by the average spatial orientation of all segments between the beads. It then turns out that the average diffusion tensors of the end beads have the same symmetry as the stress tensor in the liquid, e.g. $D_{13} = D_{23} = 0$ (cf. equations (4.1.10) or (4.3.27)). There are two reasons why we expect this to be a better and more realistic model. The first is the need for a self-consistency condition in the melt, but possibly not in very dilute solutions. The molecular theories predict various anisotropic properties of the liquid in flow (stress, birefringence, etc.). In the melt we have to assume that by summing over all chains, we simultaneously arrive at the average properties of the medium surrounding the chains. If the chains become distorted, it is only logical that the medium becomes anisotropic and hence the diffusion should not, in general, be isotropic except possibly for small deformations. Some authors^{26,27} believe that this is the cause of the Mooney C_2 term in rubber elasticity and point out that C_2 decreases with increasing swelling by solvent. The second ground for relaxing spherical symmetry with the diffusion tensor is the simple observation that a chain is a flexible linear string and it is more logical to use the symmetry of the hydrodynamic resistance of a cylinder or ellipsoid to define the components of the diffusion tensor of a typical segment.

Case A

The diffusion equation (4.2.8) for simple steady shear flow reads:

$$-qx_2 \frac{\partial \psi}{\partial x_1} - \frac{D}{kT} \left[\frac{\partial}{\partial x_1} (F_1 \psi) + \frac{\partial}{\partial x_2} (F_2 \psi) + \frac{\partial}{\partial x_3} (F_3 \psi) \right] + D \left[\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial x_3^2} \right] = 0 \quad (4.3.15)$$

This is multiplied in turn by $x_1 x_2$, x_2^2 , and x_3^2 , and integrated through space with the same assumption as in the last section. This gives:

$$q\langle x_2^2 \rangle + \frac{D}{kT} \langle x_1 F_2 + x_2 F_1 \rangle = 0 \quad (4.3.16)$$

$$\frac{D}{kT} \langle x_2 F_2 \rangle + D = 0 \quad (4.3.17)$$

$$\frac{D}{kT} \langle x_3 F_3 \rangle + D = 0 \quad (4.3.18)$$

From the last two equations it is seen that for steady shearing flow $\langle x_2 F_2 \rangle = \langle x_3 F_3 \rangle = \text{constant}$. On comparison with (4.1.1), we may conclude that in this model the second normal stress difference, $p_{22} - p_{33}$, will always be zero, even when the spring force is an arbitrary non-linear function. When this is true, then the model fails by not giving the required behaviour. A further objection to modifications on these lines is that the stress-optic relation will break down.

Case B

We start again with the equation for a dumbbell, but write it out for the general case when $\underline{F}$ is not specified and D_{ij} has the symmetry of stress (the assumption is not necessary, but can be proven). In full for steady shear flow:

$$\begin{aligned} & \frac{\partial}{\partial x_1} (D_{11} \frac{\partial \psi}{\partial x_1} + D_{12} \frac{\partial \psi}{\partial x_2}) + \frac{\partial}{\partial x_2} (D_{12} \frac{\partial \psi}{\partial x_1} + D_{22} \frac{\partial \psi}{\partial x_2}) + \frac{\partial}{\partial x_3} D_{33} \frac{\partial \psi}{\partial x_3} - qx_2 \frac{\partial \psi}{\partial x_1} - \\ & -kT \left[\frac{\partial}{\partial x_1} (D_{11} F_1 + D_{12} F_2) \psi + \frac{\partial}{\partial x_2} (D_{12} F_1 + D_{22} F_2) \psi + \frac{\partial}{\partial x_3} D_{33} F_3 \psi \right] = 0 \end{aligned} \quad (4.3.19)$$

We now substitute the rubber elasticity expression for the force in the chain (4.1.13) and assume that the diffusion tensor has been pre-averaged for the gradient q . As in the preceding cases, we multiply the above by $x_1 x_2$, x_1^2 , x_2^2 and x_3^2 in turn and integrate over all space. This yields the following set of equations:

$$q\langle x_2^2 \rangle - 2\mu(D_{11} + D_{22}) \langle x_1 x_2 \rangle - 2\mu D_{12} \langle x_1^2 + x_2^2 \rangle + 2D_{12} = 0 \quad (4.3.20)$$

$$q\langle x_1 x_2 \rangle - 2\mu D_{11} \langle x_1^2 \rangle - 2\mu D_{12} \langle x_1 x_2 \rangle + D_{11} = 0 \quad (4.3.21)$$

$$-2\mu D_{12} \langle x_1 x_2 \rangle - 2\mu D_{22} \langle x_2^2 \rangle + D_{22} = 0 \quad (4.3.22)$$

$$-2\mu D_{33} \langle x_3^2 \rangle + D_{33} = 0 \quad (4.3.23)$$

From the last of these it follows that, as with the simple dumbbell, $\langle x_3^2 \rangle$ remains unchanged by the flow. Yet, the above system of equations gives unequal normal stresses p_{22} , p_{33} and refractive indexes n_{22} , n_{33} . The stress-optic law is included by virtue of the assumption concerning the chain force. Let us now

estimate the ratio of the refractive index difference $n_{22} - n_{33}$ to $n_{11} - n_{33}$. To begin, (4.3.23) is combined with (4.3.22) and (4.3.21) in turn.

This yields:

$$- 2\mu D_{12} \langle x_1 x_2 \rangle + 2\mu D_{22} \langle x_3^2 - x_2^2 \rangle = 0 \quad (4.3.24)$$

$$q \langle x_1 x_2 \rangle - 2\mu D_{12} \langle x_1 x_2 \rangle + 2\mu D_{11} \langle x_3^2 - x_1^2 \rangle = 0 \quad (4.3.25)$$

whence the ratio of the two differences is:

$$\frac{n_{22} - n_{33}}{n_{11} - n_{33}} = \frac{\langle x_2^2 - x_3^2 \rangle}{\langle x_1^2 - x_3^2 \rangle} = - \frac{D_{11}}{D_{22}} \frac{2\mu D_{12}}{2\mu D_{12} - q} \quad (4.3.26)$$

According to the assumption of cylindrical symmetry, D is given by:

$$D_{ij} = D_2 \delta_{ij} + (D_1 - D_2) \langle \frac{x_i x_j}{r^2} \rangle \quad (4.3.27)$$

where D_1 and D_2 are proportional to the principal diffusivities of a typical random link. D_1 is proportional to the diffusivity of a link along its axis, and D_2 is proportional to the diffusivity perpendicular to its axis. The above equation is a general relation for the components of a tensor of cylindrical symmetry onto a cartesian coordinate system. When the coil is undistorted $\langle x_i x_j / r^2 \rangle = \frac{1}{3} \delta_{ij}$ and the diffusion of the end bead is spherically symmetric with $D_{ij} = [(D_1 + 2 D_2)/3] \delta_{ij}$. In this case, the diffusion of the end bead is determined by the average value of the segment diffusivities. On flow the coil becomes distorted and the spherical symmetry is lost. In order to calculate this case, the average product of the direction cosines $\langle x_i x_j / r^2 \rangle$ is approximated to $\langle x_i x_j \rangle / \langle r_0^2 \rangle$. This is a fair approximation as long as the coil distortion remains small. The limiting value for D_{12} as q approaches zero is then given by:

$$D_{12} = (D_1 - D_2) \frac{\langle x_1 x_2 \rangle}{\langle r_0^2 \rangle} \quad (4.3.28)$$

In the same limit $\langle x_1 x_2 \rangle$ is given by (see Eq. (4.3.6)):

$$\langle x_1 x_2 \rangle = \frac{q \langle x_2^2 \rangle}{4\mu \langle D \rangle} \quad (4.3.29)$$

where $\langle D \rangle = (D_1 + 2 D_2)/3$. The ratio of the refractive index differences can then be evaluated easily and the result is:

$$\frac{n_{22} - n_{33}}{n_{11} - n_{33}} = - \frac{D_1 - D_2}{D_1 + 5D_2} \quad (4.3.30)$$

There is now needed an expression for the ratio of the diffusivities D_1 to D_2 . This ratio is determined by the ratio of the hydrodynamic resistances of a random link when it is translated either parallel or perpendicular to its axis. Account has to be made of the fact that the diffusivity of a link is inversely proportional to its hydrodynamic resistance. In the present case the ratio D_1/D_2 was found by modeling a link to an infinitely long but thin cylinder. This gives the same result, as would be obtained by modeling the link to an ellipsoid of infinite axial ratio. In this limiting case D_1 is equal to $2D_2$. More general results for ellipsoids and cylinders of various shapes are to be found in the literature^{28,29}).

The ratio of the refractive index differences is then:

$$\frac{n_{22} - n_{33}}{n_{11} - n_{33}} = -\frac{1}{7} \quad (4.3.31)$$

If the link were modeled to a cylinder with length to diameter ratio of 10:1, which is more reasonable considering that Kuhn's random link often contains about ten monomer units, the ratio of the refractive indexes should be about -0.1.

From (4.3.31) we see that, if the normal stress difference ($p_{11} - p_{33}$) or the refractive index differences ($n_{11} - n_{33}$) are positive, it then follows that the differences $n_{22} - n_{33}$ and $p_{22} - p_{33}$ are negative. Later it will appear that (4.3.31) gives the correct sign and magnitude found in experimental measurements both of normal stress differences and of refractive index differences.

According to the above, the ratio of the differences should be independent of concentration, molecular weight, and molecular weight distribution of the polymer. It should only depend on the "stiffness" of the component random links.

It is interesting to compare these results with the behaviour of rigid particles of cylindrical symmetry, the subject of extensive study^{24,25,30}). For this case, the stress optical law does not hold when the extinction angle deviates from 45°. Giesekus²⁴) has examined the normal stress differences in the second order region and found for the two extremes of needles (ellipses of infinite axial ratio) and platelets (infinitely small axial ratio), $(p_{33} - p_{22})/(p_{11} - p_{22})$ lay between 1/6 and 0.4 with a minimum of 0.08 at an axial ratio of 6:1. The corresponding ratios for the refractive index differences have never been given. From calculations using the theory of Peterlin and Stuart³¹), it can be shown that the ratio should vary monotonically between 2.5 (plates) and 0.4 (needles). Thus, for rigid particles, the theoretical ratio of the normal component differences is markedly different for stress tensor components and refractive index tensor components. In fact, the ratio from the optical components would be the most suitable in determining shapes of particles, should one be required to do this by rheological means.

The extended dumbbell model also predicts a weak non-Newtonian viscosity and normal stresses which show a more complicated dependency on q than the strictly quadratic one in the original dumbbell model. However, we do not believe that such a linear theory can be used to explain non-Newtonian behaviour

(see Section 6.2). We only suggest the model, as it gives possible mechanism for the inequality of the p_{22} and p_{33} in and near the second order region. The origin of non-Newtonian viscosity and other non-linear effects should be sought elsewhere.

When consideration is made of the viscoelastic parameters G' and G'' , it appears that dumbbell models can only supply a limited number of relaxation mechanisms whilst polymer solutions and melts require a wide spectrum of relaxation times for a satisfactory phenomenological description of experimental results.

We now pass on to the most well-known of polymer models which possesses the latter possibility.

4.4 The Rouse Model

In this model the macromolecule is represented by a set of N identical beads joined by $N-1$ identical segments¹⁵). The number of real atomic units between each bead is supposed so great that Gaussian chain statistics may be assumed to hold between the beads. As in the dumbbell model, all hydrodynamic effects are assumed to act on the beads via an isotropic diffusion tensor. The model, while often associated with the name of Rouse, seems to have been developed to the same degree, but independently by others^{32,21}). Originally the theory was developed to describe the behaviour of dilute solutions. When applied to melts it will be referred to as the modified theory of Rouse. The application to melts is essentially based on the interpretation of entanglements due to Ferry and others^{33,34,35}) in which entanglements are supposed to contribute an excess friction to segments of polymer molecules. Thus, each molecule behaves at low deformation rates as if it were immersed, independently of the other molecules, in a medium of increased viscosity.

The mean force acting between beads p and $p+1$ is given by the linear relation:

$$F_{p,p+1} = - 2\mu kT(r_p - r_{p+1}) \quad (4.4.1)$$

where 2μ now equals $3/b^2$; b^2 is the mean square distance between consecutive beads. The force acting on the p bead originating from the segments $p-1$ to p , and p to $p+1$, is then represented by the vector equation:

$$\underline{F} = - 2 kT \underline{A} \cdot \underline{r} \quad (4.4.2)$$

where $\underline{A}$ is the interaction tensor of order N with components

$$\begin{aligned} A_{11} &= A_{NN} = 1 \\ A_{ii} &= 2 ; i \neq N, 1 \\ A_{ij} &= -1 ; |i-j| = 1 \\ &= 0 ; |i-j| > 1 \end{aligned} \quad (4.4.3)$$

The matrix A is basic and familiar to the theories of linear systems. Thus A is associated with the vibrations of uniformly weighted strings³⁶⁾ and vibrations in crystal lattices³⁷⁾. It has been humorously suggested that A stands for Archimedes³⁸⁾. Owing to the interaction term, the diffusion equation is not readily soluble. Solution is achieved by use of a coordinate transformation which diagonalises A. The transposed forces are then used in the diffusion equation.

When the procedure is followed, the distribution function ψ can be written in the form of a product of distribution functions ψ_p for each normal mode.

$$\psi = \Pi \psi_p \quad (4.4.4)$$

Each ψ_p is governed by a diffusion equation of the dumbbell type:

$$\text{Div}[-\nabla \psi_p + 2\mu \lambda_p \underline{D} \underline{r}_p \psi_p + D \text{grad } \psi_p] = 0 \quad (4.4.5)$$

where λ_p is a diagonal element of the transformed matrix A and for large N:

$$\lambda_p = \frac{p^2}{N^2} \pi^2 \quad ; p = 1, 2, 3 \dots \quad (4.4.6)$$

By comparison with the results of the previous Section 4.3, it is evident that the model is characterised by a distribution of relaxation times:

$$\tau_p = (4 \mu D \lambda_p)^{-1} \quad (4.4.7)$$

With the omission of a hydrostatic pressure component, the components of the stress tensor are:

$$p_{12} = q \sum_m \frac{RTc_m}{M_m} \sum_{p=1}^N \tau_{pm} \quad (4.4.8)$$

$$p_{11} = 2q^2 \sum_m \frac{RTc_m}{M_m} \sum_{p=1}^N \tau_{pm}^2 \quad (4.4.9)$$

$$p_{22} = p_{33} = 0 \quad (4.4.10)$$

In view of the stress-optical relation which immediately follows from the model, the refractive index components are not given.

To obtain the components of the dynamic viscosity at frequencies ω , the quantity $\partial \psi / \partial t$ in (4.2.3) is not set equal to zero. The determination of the stress components follows a similar course to the steady shear case. When this is done, the dynamic moduli are found to be:

$$G''(\omega) = \sum_m \frac{RTc_m}{M_m} \sum_p \frac{\omega \tau_{pm}}{1 + \omega^2 \tau_{pm}^2} \quad (4.4.11)$$

$$G'(\omega) = \sum_m \frac{RTc_m}{M_m} \sum_p \frac{\omega^2 \tau_{pm}^2}{1 + \omega^2 \tau_{pm}^2} \quad (4.4.12)$$

In the limiting case of zero frequency, a simple relation results between the measurable quantities of steady and oscillatory shearing.

$$p_{12} = G''(\omega), \quad q = \omega \text{ as } \omega \rightarrow 0 \quad (4.4.13)$$

$$p_{11} - p_{22} = 2G'(\omega), \quad q = \omega \text{ as } \omega \rightarrow 0 \quad (4.4.14)$$

The above result is well-known and is quite general for simple (i.e. unstructured) liquids, as it can be obtained from more general considerations³⁹.

The relaxation times are found by combining (4.4.6) and (4.4.7):

$$\tau_p = N^2 / 4\mu D \pi^2 p^2 \quad (4.4.15)$$

In the model the diffusion constant D , the segment length b , and the number N of segments, are all adjustable parameters as they cannot be independently chosen. We expect the number of segments to be proportional to the molecular weight. The relaxation times are therefore written for each species m .

$$\tau_{pm} = f M_m^2 p^{-2} \quad (4.4.16)$$

where f is a parameter determined by D and the chosen relation between M , N and b . As

$$\sum_{p=1}^{\infty} p^{-2} = \frac{\pi^2}{6}$$

the shear stress becomes:

$$p_{12} = q c R T f M_w \pi^2 / 6 \quad (4.4.17)$$

This result differs from the dumbbell result only by a numerical factor. The shear stress and hence viscosity, should be proportional to the concentration and the weight average molecular weight. From experiments it is known, that the viscosity is not such a simple function of the molecular weight. At low degrees of polymerization (less than 600), the viscosity is indeed roughly proportional to M , but at higher degrees of polymerization it is proportional to a higher power of the molecular weight, usually the 3.4 power. To overcome this difficulty it must be assumed that f is also a function of the molecular weight. Experimentally, it is found that η is determined mainly by $M_w^{4.0, 4.1, 4.2}$,

although with some very broad distributions higher averages of the molecular weight distribution may play a role⁴³⁾. The correct dependency of η on the molecular weight is obtained by assuming f is proportional to $M_w^{2.4}$ in the higher molecular weight region.

For the normal stress difference one finds:

$$P_{11} - P_{22} = 2q^2 cRT f^2 M_z + 1 M_z M_w \pi^4 / 90 \quad (4.4.18)$$

The steady shearing compliance J_e is obtained by combining (1.3.6), (4.4.18) and (4.4.17):

$$J_e = \frac{P_{11} - P_{22}}{2 P_{12}^2} = \frac{2}{5} \frac{M_z + 1 M_z}{M_w cRT} \quad (4.4.19)$$

For melts, the concentration is replaced by the density ρ . When the melt has a narrow distribution of molecular weights, the compliance should read:

$$J_e = \frac{2}{5} \frac{M}{\rho RT} \quad (4.4.20)$$

J_e should not depend on the f factor. Again the only difference from the dumbbell model turns out to lie in a numerical constant. (For the dumbbell, 2/5 is replaced by unity.)

The measurement of the steady state compliance J_e is now a favoured way for checking molecular theories for slow flow and small, cyclic, deformation behaviour. The viscosity is no longer used since its application needs the interpretation of f in (4.4.17). Some earlier authors did this successfully⁴⁴⁾ by reducing the problem of f to that of an atomic friction factor which, however, remained empirical. The use of J_e instead of the viscosity avoids any interpretation of f since f is eliminated.

There is no longer great optimism for applying the molecular theories in their present form to the flow of melts. Following the initial investigations of Ferry³⁴⁾ and coworkers, there was considerable hope that the modified Rouse theory was applicable to melts. Indeed, it was found with some melts that J_e followed the molecular weight behaviour given by the modified theory - polyvinyl acetate^{45,46)} and polymethyl methacrylate⁴⁷⁾. Certain moderately concentrated solutions also seemed to obey the predicted behaviour^{48,49,50)}. These early hopes were dashed when polystyrene came to be examined.

As the nature of the described theory is semi-empiric, a short discussion of recent mechanical experiments seems justified. The Japanese investigators have been particularly active. Dynamic testing has been the popular mode of investigation. In one study, Onogi and coworkers found that for narrow distribution polystyrenes⁵¹⁾ η_0 was proportional to $M^{3.7}$ and J_e to M^0 for samples with molecular weights higher than a critical molecular weight M_c^* . J_e was proportional to M for molecular weights lower than M_c^* . In this region, agreement with the Rouse theory was achieved but the proportionality constant was incor-

rect by a factor five.

In a further investigation, this time on blends⁵²⁾, the same group found that η_0 was determined by M_w , but that J_e was proportional to w_2^2 where w_2 is the weight fraction of the highest molecular weight component. They also concluded that the low molecular weight component in binary blends does not contribute to J_e in the high concentration region, even when their molecular weight exceeds M_c . This means that the basic rule, given by (4.1.2) might be invalid.

Results of many J_e investigations on polystyrene melts are given in Fig. 4.1. Other materials have been investigated in individual papers^{53,54,55)}, but

Fig. 4.1 The steady shearing compliance as function of molecular weight for polystyrenes of narrow molecular weight distribution.

Drawn line ... Rouse theory.

o ... Ref.⁵¹⁾; □ ... Ref.⁵⁶⁾; ● ... Ref.⁵⁷⁾; △ ... Ref.⁵⁸⁾;

▲ ... Ref.⁵⁹⁾.

it is only with polystyrene that extensive work has been carried out allowing cross-checking of different methods. In Fig. 4.1 data are shown from stress relaxation in tensile tests⁵⁶⁾; from dynamic moduli with a concentric cylinder viscometer⁵¹⁾, and with a cone-and-plate^{57,58)}; and, from the steady shear behaviour of the shear stress and the normal stress difference⁵⁹⁾. Values of J_e from the latter work were increased by a factor two in order to correspond with the definition of J_e used in this work. The above list is by no means exhaustive. When all results are placed together in the above manner, the general result is a little muddy, but a census of opinion is present. J_e is independent of the molecular weight above a certain critical molecular weight. Below this critical weight, J_e is roughly proportional to M in the manner demanded by the

theory.

Graessly has recently⁶⁰⁾ proposed a modification of the theory to overcome the difficulty. His main point seems to be that in applying the Rouse Theory to melts (entangling systems), account should be made for the differing friction which entanglements have, dependent on their position. Thus, the diffusion coefficient is not completely smoothed and he chooses $D_{ij} = D(p)\delta_{ij}$; where p is the bead number. He obtained an expression for J_e in the form $J_e = 0.7M_e/\rho RT$ for all high molecular weight polymers. This leads to a value of J_e for polystyrene which is too small by a factor of about two only. He also obtained a dependency on the polydispersity weaker than the original theory: J_e proportional to M_z/M_w instead of $M_{z+1}/M_z M_w^2$. According to his own remarks, the Rouse theory gives a better description of the influence of polydispersity than the modified theory does⁶⁰⁾.

4.5 Molecular-Phenomenological Theories

In this section, mention is made of a few theories developed particularly to describe non-Newtonian aspects of polymer melt flow. Characteristic of the theories is a mixture of intuitive reasoning and molecular concepts; "pure" statistical premises are not present.

Graessly Model: Graessly⁶¹⁾ used the concept of entanglements for an intuitive development of non-Newtonian flow. In this he did not use the rotation of the molecules, as had been done by Bueche⁶²⁾, but rather, the changing distances between molecules. Since the kinetics of junction formation and breakdown are unknown, Graessly took a mechanistic view. In the shear field, when the molecules are close, entanglements can form. After molecules pass one another, disentanglement must occur. For an entanglement to be reformed, molecules must lie within reach of one another and remain within reach for a sufficient length of time. With increasing shear rate, this "contact time" decreases and entanglements with long diffusion times are not re-formed. The entanglement density decreases and consequently, the viscosity decreases. To specify the model, Graessly used diffusion times, obtained from the Rouse model applied to the melt. In order to satisfy the needs of self-consistency, the diffusion times are a function of the shear rate, q , and are determined by the viscosity of the melt at that shear rate.

As a result of these considerations, the limiting behaviour at high shear rates should be given by the relation: $\eta(q) \propto q^{-3/4}$.

In an ensuing development⁶³⁾, Graessly also considered the possibility that the friction factor would decrease during flow. For this latter model, the following limit relation was obtained for the high shear rate region: $\eta(q) \propto q^{-9/11}$. Alternatively, the limit relations for the viscosity can be re-phrased as limit relations for the "power law" flow curve. The exponent in the relation $q \propto p_{12}^n$ should, according to the latter version, be less than 5.5. For some systems, e.g. PVC gels, rubbers, and very high molecular weight polystyrene, exponents higher than 5.5 are often found.

In both of the models, the second normal stress difference ($p_{22} - p_{33}$) should be zero. In the first model, $p_{11} - p_{22}$ should remain proportional to the square of the shear stress. In the section on results, it will be seen that

this is a feature of polystyrene melts (but not of many other systems). The latter model of Graessly makes no pronouncement on $p_{11} - p_{22}$ behaviour.

Schroff⁶⁴⁾ claims that for the latter model, the results of Graessly may be put in the convenient form:

$$\eta(q) = \int_{-\infty}^{\infty} H(\tau) K(\tau q) d\tau \quad (4.5.1)$$

where $K(\tau q)$ is a kernel, determined by the changing number of entanglements and the changing diffusion constant.

Maximum Energy Model: Recently, Booij⁶⁵⁾ proposed an energy threshold model to account for non-linear behaviour in polymer fluids. The basic postulate is: "A mode of relaxation characterized by a time τ cannot store an amount of free energy greater than kTb^2 where b is a constant. The mode disappears when this limit value is exceeded during the deformation process". The parameter b was assumed independent of τ . The physical picture in the model is that modes with long relaxation times are more deformed than modes with short relaxation times. As an example, one imagines that an entanglement between two molecules which happens to be far from the chain ends of both molecules, will take longer to diffuse out than an entanglement near their periferies. Owing to the longer diffusion time of deeply located entanglements, chains connecting these entanglements become more highly deformed. Eventually, the chain forces exceed the entanglement's strength. Consequently, the entanglement is destroyed.

The model thus resembles the Graessly model. However, the maximum energy model has advantages, in that it is more general, and detailed dynamics of chain motion do not need to be considered. Moreover, it may be applied to non-polymer systems.

The practical problem is to relate b to measurable quantities. This was tackled by considering a generalisation of the Rouse-Bueche approach and by using solutions of the diffusion equation to calculate the increase of the free energy of a mode. For the special case of steady shear flow, there was found:

$$\Delta F(\tau) = q^2 \tau^2 kT < kTb^2 \quad (4.5.2)$$

where $\Delta F(\tau)$ is the increase of the free energy over the undisturbed state of the considered mode. The influence of volume changes has been neglected in the above. The consequence of the model in the case of steady shear flow is, that an upper limit is set to the intervals over which the integrals for the flow quantities are taken. The formulae for the shear stress and the first normal stress differences are⁶⁵⁾ (cf. Eqs (1.3.2) and (1.3.3)):

$$p_{12} = q \int_0^{\tau_m} H(\tau) d\tau \quad (4.5.3)$$

$$p_{11} - p_{22} = 2q^2 \int_0^{\tau_m} H(\tau) \tau d\tau \quad (4.5.4)$$

where τ_m is the maximum permitted relaxation time:

$$\tau_m = b/q \quad (4.5.5)$$

Ajroldi, Garbuglio and Pezzin⁶⁶⁾ suggested earlier that the integral expression in (4.5.3) would be a suitable quantity for the differential viscosity dp_{12}/dq .

The above model can give a fair description of non-linear behaviour including stress overshoot*. However, as appears from the few studies made⁶⁵⁾, simple termination of the relaxation spectrum at a particular value τ_m is not consistent with both the gradient dependency of the shear stresses and the normal stresses. For example, a more gradual truncation is possible, yielding the same viscosity function and a better agreement with the gradient dependency of the normal stresses.

In addition to the above described model, other rupture models exist. The Leonov thixotropic model⁶⁷⁾ and the Simmons-Tanner model⁶⁸⁾ are examples. It appears that the results of these theories can also be put in the form of (4.5.3) and (4.5.4).

The application of any kind of truncation procedure is equivalent to the introduction of a shape function $K(q\tau)$ in the integrand. Integration is retained over the whole time scale and $K(q\tau)$ ensures that the contributions of the longer times become progressively smaller.

$$p_{12} = q \int_0^{\infty} H(\tau)K(q\tau) d\tau \quad (4.5.6)$$

$$p_{11} - p_{22} = 2q^2 \int_0^{\infty} H(\tau)K(q\tau)\tau d\tau \quad (4.5.7)$$

The idea of introducing a kernel into the expressions from the linear theory in order to describe non-linear behaviour is not new. Various proposals for suitable forms for $K(q\tau)$ have been given, including suggestions using the Ree-Ehring theory for rate processes^{66,69-71)} and the Graessly theory described previously^{63,64)}.

In our final remarks we wish to point out that the theories described in this section, are essentially linear theories since the postulates on which they are based, are linear postulates. In the Graessly theory, for instance, the coil deformation and orientation are ignored. This is perhaps justified by the experimental fact that polymer melts retain a linear behaviour up to very

*Stress overshoot is a phenomenon associated with experiments where a constant flow gradient is suddenly applied. At low rates of applied shearing, the stresses rise monotonically to equilibrium. At high shear rates, the stresses rise and overshoot the equilibrium value before decreasing to equilibrium (if obtainable). The phenomenon is particularly associated with low density polyethylene.

high deformations in dynamic testing. Nevertheless, the non-Newtonian flow is obtained by a trick which may or may not have a sound basis in a suitably modified form of the diffusion equation. By these remarks we only mean that these theories are based on ad hoc assumptions which need to be experimentally evaluated for a true assessment of their merits. It is always possible that the approach will give a good description of experimental findings and can be of assistance in the classification of materials.

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5. Results

5.1 The Stress-Optical Law

We recall the stress-optical law as developed by Maxwell and Neumann, where for simple shear (Section 1.4) the results can be expressed by the relations:

$$\Delta n \sin 2\chi = 2 n_{12} = 2 C p_{12} \quad (5.1.1)$$

$$\Delta n \cos 2\chi = n_{11} - n_{22} = C(p_{11} - p_{22}) \quad (5.1.2)$$

$$n_{22} - n_{33} = C(p_{22} - p_{33}) \quad (5.1.3)$$

Lodge¹⁾ emphasized in his original proposal for the stress-optical law (as applied to polymeric, amorphous liquids) that the relation rests on two hypotheses. One is that the off-diagonal components of the optical and the mechanical tensors are directly proportional to one another. The other is that the mechanical and optical tensors are coaxial. The first has been checked in this work for many materials in steady shear flow. This was achieved by examining the constancy of the ratio $\Delta n \sin 2\chi / 2p_{12}$. As the theory required, this ratio was found to be independent of shear rate, molecular weight, and molecular weight distribution and agreed with results on elastomers and dilute solutions of the same polymer. The molecular weights were sufficiently high ($> 20,000$) for the avoidance of short chain effects. The second hypothesis has also been checked for a few cases where mechanical measurements were kindly made available to this author by other authors.

All measurements were made with cone-and-plate apparatuses. Most of them took place in a shear rate region not far from the Newtonian region of viscosities (exceptions are the high density polyethylenes of broad molecular weight distribution).

At present, there do not exist any means of measuring the normal stresses $p_{11} - p_{33}$, etc., in the region of shear stresses higher than about 10^4 N/m². It is, therefore, not possible to check the stress-optical relation at shear stresses higher than this. However, indirect evidence derived from measurements of frozen stresses and birefringences in injection moulding will be given,

5.1.1 The Constancy of $\Delta n \sin 2\chi / 2p_{12}$ in Steady Shearing

Polystyrenes

The following materials of narrow molecular weight distribution have been measured: Pressure Chemical 3a, 6a, and 7a, and Dow S111. The following polymers of relatively broad molecular weight distribution were also investigated: Dow Styron 666, Styron 678, and BASF 3. It was not possible to measure every material at one given temperature, owing to the extreme range of viscosities involved. Where possible, a standard temperature of 190 °C was used. The low

molecular weight polymers were measured at a lower temperature than this, and the high molecular weight polymers were measured at a higher temperature.

The optical equivalent to stress overshooting (see Section 4.5: Maximum Energy Model) did not appear to be present with any of these materials. The upper limit to the experimental shear rate range was imposed by depolarization which was probably due to parasitic gradients at the windows. The shear stress vs shear rate relations were obtained with a slit apparatus (Section 2.3). It was usually possible to measure the viscosity with the slit down to about 0.1 s^{-1} . For this purpose, a specially made electronic pressure gauge with a range 0-15 bar, was used. In some cases, the Newtonian viscosity was obtained by extrapolation and in others, it was measured. The results on the polystyrenes of narrow molecular weight distribution are given in Fig. 5.1. The range of the molecular weights was 50,000 (7a) to 860,000 (6a). Shown in each figure is the course of the viscosity and the absolute value of the ratio

$$C = \Delta n \sin 2\chi / 2p_{12}$$

as a function of the shear rate. In fact, Δn is negative for polystyrene, when χ is defined as in Section 1.4. It is seen that, in every case, the ratio is a constant, independent of molecular weight (and temperature). However, it is also to be noticed that at the highest shear rates, which could be used in the cone-and-plate apparatus for birefringence, the steady shearing viscosity does not deviate significantly from the viscosity at zero shear rate. With these polystyrenes of narrow molecular weight distribution it was not possible to measure the birefringence and the extinction angle far into the region of non-Newtonian flow. Possibly as a consequence, the term $\sin 2\chi$ did not make a significant contribution to the constancy of the ratio $\Delta n \sin 2\chi / 2p_{12}$, as the extinction angle deviated by less than 15° from 45° . Thus, these particular results do not form a strong evidence for the general applicability of the stress-optical relation. On the other hand, results with the commercial polystyrenes Styron 666, Styron 678, and BASF 3, which are shown in Fig. 5.2, do. These materials have a fairly wide distribution of molecular weights with M_w/M_n ranging from 2 to 5 (Table 3.2). We again find that the quantity $\Delta n \sin 2\chi / 2p_{12}$ is independent of the gradient and has, for Styron 678, values near to those found for the polystyrenes of narrow molecular weight distribution. These commercial polymers are distinguished by the possibility of demonstrating the constancy of the ratio $\Delta n \sin 2\chi / p_{12}$ well into the region of non-Newtonian flow. The term $\sin 2\chi$ also makes a significant contribution to the constancy of the mentioned ratio, as the extinction angle deviates by up to 25° from 45° . The stress-optical coefficient, C , of Styron 666 and BASF 3, was significantly lower than that of the other polystyrenes ($4.1 \text{ nm}^2/\text{N}$ compared with about $5 \text{ nm}^2/\text{N}$). It is possible that the lower value is due to the presence of various processing aids which associate with the chains to alter their effective anisotropy. The values for C found here, are in agreement with the sparse measurements of C from tensile experiments with polystyrene elastomers^{2,3}, and with many results obtained with solutions of polystyrenes in matching solvents (solvents of the same refractive index)⁴⁻⁵.

Fig. 5.1 The steady flow viscosity (open symbols) and the absolute value of the stress-optical coefficient (filled symbols) for polystyrenes of narrow molecular weight distribution as a function of the gradient q .

Fig. 5.2 The steady shearing viscosity (open symbols) and the absolute value of the stress optical coefficient (filled symbols) for commercial polystyrenes, as a function of gradient q .

□, ■ ... Styron 678; ○, ● ... Styron 666; △, ▲ ... BASF 3.

The following polymers have been measured: HDND and HDBD (high density with respectively narrow and broad molecular weight distributions), LDND and LDBD (low density polymers) and material A (also low density). The birefringence measurements in the cone-and-plate apparatus were discontinued when either depolarization precluded measurement or stationary results were not obtained within a reasonable time (15 minutes at each speed). The latter problem often occurs with low density polyethylenes when the shear rate is too high and stress overshoot occurs. For the above materials, the dependency of the viscosity on the shear rate was obtained with cone-and-plate apparatus of the Kepes type. The only exception was material A, where a Weissenberg apparatus was used. The data are also to be found in the literature^{6,7}). The temperature of measurement was mainly 150 °C. As with the polystyrenes, the quantity $C = \Delta n \sin 2X/2p_{12}$ has been plotted against the shear rate along with the viscosity function. In Figs 5.3 and 5.4, the constancy of C can be seen despite a great variation in molecular weight, molecular weight distribution and non-linear behaviour. For HDBD, measurements were only possible in the non-Newtonian region of viscosity.

The low density polyethylenes of Fig. 5.4, have different molecular weight distributions, but similar flow behaviour (see Table 3.2). The flow behaviour of linear polymers, such as the high density polyethylenes, is much more sensitive to variations in the molecular weight and its distribution. This fact is generally ascribed to the chain branching in low density polyethylene. In the figure, the coefficient C appears to have a value somewhat smaller than the value for the high density polyethylenes (see also Table 5.1). The lower value could also be a result of branching in low density polyethylenes. If true, we expect the decrease with respect to the high density polymers to be proportional to the number of branches since the segment polarizability at a branch root will be more optically isotropic than at other places along the chain. This appears to be true, as the present author has found a linear relation between the stress-optical coefficient and the branching index of a series of low density polymers.

Fig. 5.3 The viscosity (open symbols) and stress-optical coefficient (filled symbols) for two high density polyethylenes of widely differing molecular weight distributions.

Fig. 5.4 The viscosity (open symbols) and stress-optical coefficient (filled symbols) for low density polyethylenes of widely differing molecular weight distributions.

The other materials measured were two polypropylenes and a polydimethylsiloxane. The polypropylenes were of similar weight average molecular weight, but of different molecular weight distribution. As a result, their zero shearing viscosity was similar, but their non-linear behaviour and normal stresses were distinctly different⁸⁾. The results are shown in Fig. 5.5. The scatter in the viscosity measurements is a consequence probably of oxygen attack for which polypropylene is extremely susceptible at high temperatures (see also Section 2.1.2). Nevertheless, it is clear as with the other polymers, that the stress-optical coefficient is constant independent of molecular weight and non-linear behaviour.

The results obtained for the silicone oil Siloprene RS, are shown in the following Fig. 5.6. The viscosities at low shear rates were kindly supplied by W. Philippoff. The result is the same as with the previous polymers: the stress optical coefficient is independent of the applied steady shearing gradient. This material has a distorted extrudate when it is pressed through capillaries at shear rates greater than about 30 s^{-1} . At this critical speed, the flow curve also shows a sharp bend. This is a general phenomenon which can be loosely called melt fracture. Most polymers show this phenomenon at shear rates higher than are experimentally available with cone-and-plate apparatuses. This material is exceptional in that such shear rates were measurable. No kind of flow instability was observed in these experiments, however.

Fig. 5.5 The viscosity (open symbols) and the stress-optical coefficient (filled symbols) as a function of the shear rate for two polypropylenes of nearly the same weight average molecular weight, but different distributions.

Fig. 5.6 The viscosity (open symbols) and the stress-optical coefficient (filled symbols) for a silicone oil. The results at low rates were supplied by W. Philippoff.

5.1.2 The Coaxiality of the Stress and Optical Tensors

Owing to the general unavailability of direct measurements of the normal stress differences, the coaxiality of the tensors could be checked for two polymers only: the two polypropylenes, and the low density polyethylene A. The normal stress differences were determined with cone-and-plate apparatuses of the Weissenberg type^{7,8)}, together with the viscosity. Displayed in Figs 5.7 and 5.8 are the extinction angle χ_o obtained in the course of the streaming birefringence experiments, and the mechanical orientation χ_m defined in terms of the shear stress p_{12} and the first normal stress difference $p_{11} - p_{22}$.

$$\tan 2\chi_m = \frac{2 p_{12}}{p_{11} - p_{22}} \quad (5.1.4)$$

The correspondence between the mechanical and the optical orientations is good and clearly justifies the application of the stress-optical relation - at least for the systems and conditions investigated.

It has to be admitted in the case of the low density polyethylene that, at higher shear rates than the ones shown, there appeared to be differences in that, at long times, the optical extinction angle was a few degrees higher than the mechanical. This appeared to be associated with the appearance of stress-overshoot with both the mechanical and the optical quantities. Under these conditions, of course, conditions of steady flow were unobtainable. It was very difficult to decide whether the results represented a physical re-

ality or could still be due to an experimental artifact (see also Section 6). Qualitatively, the behaviour of the extinction angles under these conditions, is interesting as, with high shear rates, the extinction angle tends to increase after some time instead of decrease, which is the normal behaviour.

Fig. 5.7

Fig. 5.8

The optical extinction angle, X_0 , and the mechanical orientation angle of the principal stresses, X_m , for polypropylenes (left) of narrow and broad molecular weight distribution, and for a low density polyethylene (right).

5.1.3 Indirect Evidence of the Validity of the Stress-Optical Law at High Shear Stresses

Indirect evidence was obtained for polystyrene during the course of injection moulding experiments with Styron 678⁹). Other results concerning injection moulding are discussed in a later section (5.5.2). When parallel sided strips are moulded by injection at one end, the flow is mainly shear. After the plate is ejected from the machine, processing stresses remain frozen in the material. These stresses are composed of packing stresses, which effect the density and of deviatoric stresses, which largely account for the warping of the product on ageing or heat treatment. The deviatoric stresses (shear and normal) are accompanied by frozen birefringence.

The magnitude of the shear stress frozen into the plate, can be estimated from the time course of the pressure distribution along the cavity during injection. On sectioning the plates parallel to their longest edge, and perpendicular to their largest surface, one can examine the birefringence in the 1-2 plane of the frozen flow. In this way, edge effects are avoided which would otherwise make examination of the flowing melt in the 1-2 plane difficult. The sections are placed under a polarizing microscope, with or without a surrounding medium, and the extinction angles and birefringences are measured. In white light the extinction angle is derived from the position of a sharp black line parallel to the edges. This line moves on rotation of the crossed polaroids. (The reader will note that the extinction angle could not

be sharply determined with the flowing melt - Section 2.2: Measurements in the 1-2 plane.) The results were then used to check the constancy of the ratio $\Delta n \sin 2X/2p_{12}$ as a function of the shear stress.

In the outlined experiments, the dimensions of the mould cavity were $2 \times 65 \times 300 \text{ mm}^3$; the mould temperature was 50°C ; and the melt temperature varied from 210°C to 250°C .

Typical results are shown in Fig. 5.9. The upper part shows the required pressure distribution⁹⁾ and the central part the birefringence. Behind the flow front, the material freezes first at the walls. As a result, the direct proximity of the walls shows an optical structure, more or less independent of the filling conditions, e.g. injection pressure. In the central planes of the cavity the effects of longitudinal gradients are noticeable. In this central region, the optical pattern is the most strongly influenced by any relaxation phenomena after the mould filling cycle.

Fig. 5.9 Typical results from injection moulding experiments on Styron 678. Moulding conditions: melt temperature 230°C ; mould temperature 50°C ; injection pressure 510 bar.

Upper : the longitudinal pressure distribution before the gate freezes.

Centre : birefringence distribution in the 1-2 plane for regions A, B and C of the upper figure.

Lower : distribution of the optical shear component across the section for regions A, B and C of the upper figure.

On account of these considerations it is believed that, during the mould filling process, the flow near the birefringence peak (Fig. 5.9 centre) makes the closest approximation to steady shearing flow.

The region of the peak in the birefringence pattern was therefore used to evaluate the course of the stress-optical coefficient at high shear stresses.

The distribution of the shear component $\Delta n \sin 2\chi$ is shown in the lower portion of Fig. 5.9. In the region of the peak, the extinction angle is small - between 4° and 10° in the investigated cases - and $\sin 2\chi$ is subject to considerable error. $\Delta n \sin 2\chi$ might be expected to vary linearly over the plate cross-section. This does not appear to occur. The strongest deviations from linearity are near the gate and are probably the result of back flow after the mould was filled. On occasions the back flow near the gate can be seen in the frozen birefringence pattern by the presence of secondary peaks or in the stress, by a change in sign of the pressure distribution. A full account of all these and other details cannot be given as yet. They are, of course, important for the process but not for the point to be made here.

From a series of plates made by injection at various pressures, the ratios $\Delta n \sin 2\chi / 2p_{12}$ were determined and plotted, in Fig. 5.10, against the shear stress. The latter was estimated from the frozen longitudinal pressure gradient, using the depth of the cavity and the position of the peak (cf. formula 2.5.1). The results for true steady shearing flow are also shown for comparison. Scatter with the injection moulding experiments is large, but it is clear that the ratio of the shear components is an essentially constant quantity over the whole range of shear stresses.

Fig. 5.10 The stress optical coefficient as a function of shear stress for steady shearing experiments and from the stresses and birefringence frozen in injection mouldings.

The upper shear stress limit to the measurements on injection moulded plates was about six times that with the cone-and-plate experiments. This factor would seem to be relatively small but it should be born in mind that, owing to the extreme non-linear behaviour of the viscosity function, shear rates under isothermal conditions - at 190°C - would have to range up to 10^4 s^{-1} in a laboratory apparatus to cover the same shear stress region. This cannot be achieved at present with any apparatus.

5.1.4 Temperature Dependence of the Stress-Optical Coefficient

The stress-optical coefficient C for amorphous melts is, according to the theory, a function of the structure of the monomeric units. Inspection of the expression given by the simple theory (Equation 4.1.18) shows that the coefficient may change with temperature by three mechanisms:

- 1) The ubiquitous kT factor - C should decrease with increasing temperature, but by a small amount since the temperature T is in degrees Kelvin, and often only a moderate temperature range is available.
- 2) Density changes - these alter the refractive index and the Lorentz-Lorenz factor. The influence of density changes is very small, however, and can be neglected for most work. For example taking polydimethylsiloxane, the effect is no more than 3 % in going from 20° to 190 °C.
- 3) Conformation changes altering the anisotropy of the random link - for the real polymer chain, the frequency and ordering of the rotational isomers determines the effective segment anisotropy^{10,11}). Temperature changes can be expected to alter this balance³⁸). As a consequence, the stress-optical coefficient can be temperature dependent. The exact theory can be given in a formal way only¹²). For applications, simplifications have to be made, and doubts remain as to the correctness of the basic premisses, e.g. additivity of bond polarizabilities. Nevertheless, the stress-optical method has had some use for the substantiation of proposed models for the real-chain sequencing of the rotational isomers.

As a result of changes to the isomer distribution, C may either decrease or increase with increasing temperature - ignoring the first effects 1) and 2). Three of the materials chosen for this work show the three different types of behaviour possible. The stress-optical coefficient of polystyrene is independent of temperature, that of polyethylene decreases slightly with increasing temperature, but that of polydimethylsiloxane increases with increasing temperature. The same behaviour of the stress-optical coefficient is also found by static stretching of elastomers of the same polymers^{2,13-17}).

The most striking effect is with the silicones. Figure 5.11 shows the evaluated stress-optical coefficients for the polydimethylsiloxane E302 at 22, 105 and 190 °C. For comparison, other results for elastomers from the same polymer type, but crosslinked by various methods, are also shown. A fair agreement is found between values and temperature dependencies of the stress-optical coefficient as determined by the various methods. The stress-optical coefficient of polydimethylsiloxane is small and sensitive to chemical impurities¹⁸). This latter fact may explain the dependency on the method of crosslinking and the result that C from flow birefringence is greater for Siloprene RS than for E302 (see Table 5.1).

A smaller relative change in C with temperature was found for polyethylene. For the high density type, the stress-optical coefficient decreased from $2.4 \times 10^{-9} \text{ m}^2/\text{N}$ at 150 °C to $1.8 \times 10^{-9} \text{ m}^2/\text{N}$ at 190 °C. This decrease appears to be in agreement with results obtained for elastomers of this material¹⁵).

The physical origin of the marked increase in C with increasing temperature for the silicone oil is thought to be a decrease in population of bonds in the

trans conformation. The coil expands since the corresponding increase in the number of bonds in the "gauche" position causes an increase in the chain end-to-end distance.

Fig. 5.11 Left: The stress optical coefficient for a silicone oil as a function of shear stress at $\circ$... 20 °C, $\circ$... 105 °C; ∇ ... 190 °C. Right: The stress-optical coefficient of silicone elastomers as a function of temperature. Δ ... crosslinked with 8 % "hydride" (Ref. ¹⁷); $\circ$... crosslinked by 1 % dichlorobenzoyl peroxide, giving same results as by irradiation (Refs ¹⁷ and ¹⁶); $\bullet$... this work.

The same mechanism is also thought to cause the stress-optical coefficient and the chain end-to-end distance of polyethylene to decrease with increase of temperature. This remarkable difference in behaviour between the two polymers is to be explained apparently¹⁷⁾ by the difference of the two bond angles OSiO and SiOSi, whereby the trans form of the chain is coiled-up for the silicone. The trans form of the polyethylene chain is the fully stretched chain.

Table 5.1

Stress-Optical Coefficients

material	M_w (10^5)	temp. (°C)	C ($10^{-9} \text{ m}^2/\text{N}$)
HDBD		150	2.4
HDBD		190	1.8
HDND		150	2.35
A		150	2.1
LDND	1	150	2.1
LDBD	4.2	150	2.0
PPND	5 (1)	210	0.9
PPBD	4 (1)	210	0.9
Siloprene	3.8 (2)	22	0.175
E302	7.7 (2)	25	0.135
E302	7.7 (2)	105	0.19
E302	7.7 (2)	190	0.265
Styron 666	3.7	190	4.1
Styron 678		190	4.8
BASF 3	4.1	178	4.5
BASF 3	4.1	188	4.6
BASF 3	4.1	200	4.4
BASF 3	4.1	214.5	4.2
S111	2.2	190	5
3a	3.9	200	5.2
6a	8.6	214	4.4
7a	0.51	158.5	5

(1) M_v in Decaline at 135 °C(2) M_v in Toluene at 25 °C

5.2 Intrinsic Quantities at Zero Shearing

In view of the great interest in the molecular theories, part of this work was carried out with a series of polystyrenes of narrow molecular weight distribution. The range of molecular weights was 5×10^4 to 1.8×10^6 . For practical reasons, the temperature was varied between 150 °C and 240 °C, depending on the molecular weight under examination. Measurement of each polymer at one temperature would require an apparatus capable of covering a viscosity range of nearly five decades. To convert to the isothermal standard of 190 °C, the results were adjusted with the aid of experimentally determined temperature shift factors (Section 5.3.3) from some members of the series (S111, 6a and 3a).

The zero shearing limits (intrinsic values) of the following quantities were determined:

$$A = \frac{n_{12}}{q} = \frac{\Delta n \sin 2X}{2q} \quad (5.2.1)$$

$$B = \frac{n_{11} - n_{22}}{q^2} = \frac{\Delta n \cos 2X}{q^2} \quad (5.2.2)$$

Twice the zero shearing limit of the first quantity is sometimes called the intrinsic Maxwell constant. Apart from the numerical factor, this is the optical equivalent to the zero shearing viscosity. The second quantity B is the optical equivalent of the coefficient of the first normal stress difference. Figure 5.12 shows the experimental ratios A and B as a function of the shear rate at the temperature of measurement for each member of the series. Two members of low molecular weight (51,000 and 97,000) were measurable in the region of second order flow only and, as a consequence, the ratios remained unchanged within the shear rate range. For the other, higher, molecular weights both A and B decreased with increasing gradient, but extrapolation to the second order region was still possible. The zero shear limits of A and B were then shifted to correspond to 190 °C and the results were plotted in Fig. 5.13 to show the molecular weight dependency.

From the results shown in Fig. 5.13, the following relations were empirically found to describe the relationships between the intrinsic quantities and the molecular weight:

$$\lim_{q \rightarrow 0} \frac{n_{12}}{q} = 2 \times 10^{-22} M^{3.3}, \quad T = 190^\circ \text{C} \quad (5.2.3)$$

$$\lim_{q \rightarrow 0} \frac{n_{11} - n_{22}}{q^2} = 2.2 \times 10^{-40} M^{6.6}, \quad T = 190^\circ \text{C} \quad (5.2.4)$$

The first relation corresponds well with the relation for the molecular weight dependency of the Newtonian viscosity. Fox and Flory¹⁹⁾ gave an exponent of 3.4 for the viscosity relation and other authors have given other values close to this.

Fig. 5.12 The optical equivalents of the viscosity and the coefficient of the first normal stress difference. Open symbols ... n_{12}/q , closed symbols ... $(n_{11} - n_{22})/q^2$. $\circ$... 7a, $\bullet$... 4a, $\circ$... S111, ∇ ... 1a, $\square$... 3a, $\blacksquare$... 5a, $\blacksquare$... 6a, $\blacktriangle$... 14a. For the temperatures of measurement, see Table 3.1.

Fig. 5.13 Intrinsic quantities at zero shear rate for polystyrenes of narrow molecular weight distribution. All results converted to 190 °C. $\circ$... $\lim_{q \rightarrow 0} n_{12}/q$, $\bullet$... $\lim_{q \rightarrow 0} (n_{11} - n_{22})/q^2$.

Using these results and a stress-optical coefficient of $5 \times 10^{-9} \text{ m}^2/\text{N}$ (see Table 5.1), the following relation for J_e was determined with the aid of Eq. (1.3.6):

$$J_e = 1.4 \times 10^{-5} \text{ m}^2/\text{N} \quad (5.2.5)$$

for all molecular weights.

However, the normal stress function is very sensitive to molecular weight and the applied shear gradient. It is also possible that, at the higher molecular weights, the results were not ideally extrapolated to zero shear rate. For the determination of J_e a better extrapolation method is to use the ratio of half the normal stress difference to the square of the shear stress. This ratio becomes equal to J_e in the limit of zero shear stress, yet it is far less shear rate dependent than the viscosity and normal stress coefficients individually. Figure 5.14 shows the shear rate dependency of the ratio of the corresponding optical quantities $\frac{1}{2}(n_{11} - n_{22})/n_{12}^2$, which we shall define as J_{eo} .

Fig. 5.14 The optical corollary $J_{eo} = \frac{1}{2}(n_{11} - n_{22})/n_{12}^2$ to the steady shearing compliance, plotted as a function of the shear rate q . The results show that J_{eo} is insensitive to the shear rate for these polymers of narrow molecular weight distribution, even when the viscosity is non-Newtonian.

○ 7a .. at 158 °C; ○ 4a .. at 168 °C; ▽ 1a .. at 165 °C; ● ... S111 at 196 °C; □ 5a .. at 200 °C; ■ 6a .. at 214 °C; ◻ 14a .. at 242 °C.

We find within the scatter of the measurements, independency of the shear rate, even in the region where a pronounced non-Newtonian viscosity is found (compare Fig. 5.1).

According to the results shown in Fig. 5.14, a weak dependency of J_{eo} on the molecular weight is found, which was lost by the previous analysis of the data in Fig. 5.13. J_{eo} appears to increase with molecular weight to reach a plateau

at a molecular weight of about 200,000. By a simple multiplication by the stress-optical coefficient, J_e is calculated for the plateau region to be about $1.8 \times 10^{-5} \text{ m}^2/\text{N}$, which is in good agreement with the work of others (see Fig. 4.1).

5.3 Results with the Slit Apparatus

5.3.1 The Influence of the Aspect Ratio

As a check on the important supposition that the edge effects were not of great influence, the birefringence, $n_{11} - n_{33}$, of a low density polyethylene was measured with slits A, B and C (see Table 2.1). Slit B with an aspect ratio of 30 : 1, was used for measurements at a distance of $L/a = 15$ and $L/a = 35$ from the entrance. Slit C with an aspect ratio of 12.5 : 1, was used for measurements at $L/a = 15$, whilst slit A with an aspect ratio of 10 : 1, was used for measurements at $L/a = 35$ from the entrance. Slits A and C have nearly the same aspect ratio (order of 10 : 1). It was found that the slits of aspect ratio 10 : 1 gave exactly the same results as the slit of aspect ratio 30 : 1. These results for a polyethylene are shown in Fig. 5.15. The same independency on the aspect ratio was also found for the polystyrene Styron 678. Since a very large range of non-Newtonian viscosity behaviour was covered by these two materials, it is believed that these results confirm from the experimental standpoint the sufficiency of slits of aspect ratio 10 : 1. The two curves in Fig. 5.15, indicate that, whilst the aspect ratio has no influence on the results, the distance of the measuring point from the entrance has. This is the subject of the next section.

Fig. 5.15 The influence of the aspect ratio on measurements of the 1-3 plane birefringence with slits. The two different curves were obtained by measurement at two different reduced distances from the entrance.

5.3.2 The Influence of Pre-history

As a measure of the pre-history in ducts, we may take the distance of the observers window from the entrance to the channel. However, other factors play a role as well. Such factors are for instance the method of filling or the shape of the entrance. The first point to be noted is that different materials show widely different types of behaviour in this respect. The polystyrenes examined did not show a pronounced influence of pre-history: the same birefringence was obtained when measurements were made at $L/a = 35$ or $L/a = 96$ from the entrance. For this material, the entrance effects die out at quite a short distance from the entrance. On the other hand, low density polyethylenes formed an exceptional class of materials as they often did not reach a state of equilibrium flow - even with the longest slits available. The material of Fig. 5.15 was such an example. For the determination of $n_{11} - n_{33}$ with a view to obtaining equilibrium quantities, it is therefore essential to check by measuring at two or more positions in the slit. For an examination of the changes occurring in the duct in the direct neighbourhood of the entrance, the present slit dies are unsuited. In order to get an impression of the birefringence changes near the entrance, measurements have been made with short glass capillaries mounted in a holder in the reservoir of a piston driven viscometer. The outer surface of the capillary was thus surrounded by polymer. This lessened the influence of the hydrostatic pressure on the capillary glass and at the same time almost completely nullified the lens effect of the outer surface of the capillary. The complete capillary was viewed via windows mounted in the wall of the reservoir and the birefringence determined in the usual way. With flat entrances to the capillaries, the findings had the general shape of the findings for slits. With polystyrenes equilibrium was reached, however, at very short distances from the entrance and for those measured (Styron 666 and BASF 3) this was less than 10 diameters.

With glass capillaries the field is non-uniform, but compensation can be achieved readily along the axis. In the equilibrium region this is related via a relation similar to (2.2.4) to the birefringence at the wall. For quantitative measurements glass capillaries are less suited than slits in that the results are less reproducible. The strains in the glass form one factor. The other is that glass is a bad conductor of heat, and temperature variations can more readily occur. Examples showing the monotonic decrease of the birefringence as the fluid flows along a slit and along a glass capillary, are shown in Fig. 5.16. The left hand part shows that, with the LDPE Alkathene 2, equilibrium is not reached in any slit of length less than 100 depths. The right hand part shows, on the other hand, that for the polystyrene, Styron 666, equilibrium is consistently reached within 5 capillary diameters.

In the above, the orientation decreased to an equilibrium value. This decrease is modified when the material is pressed into the duct by a screw extruder instead of by a piston as in the above examples. It is also modified when the material passes a restriction at the entrance to the capillary. When a screw extruder was used with low density polyethylene, the birefringence still decreased along the slit, but started at a lower value, later to coincide with that found in experiments with a piston driven viscometer. After passing a restriction it is even possible for the birefringence to increase in

Fig. 5.16. Left: Plotted against the reduced distance from the entrance, L/a , is the birefringence in the 1-3 plane for LDPE in slits. For practical purposes, equilibrium flow in ducts does not exist with this material.

Right: For comparison, the birefringence in the 1-3 plane for a polystyrene in a capillary. The extremely short reduced distance needed to reach equilibrium is typical of this material.

the direction of flow. In this case the equilibrium length of the capillary seems to be greater than without the restriction. Such an entrance has been used to study the orientation induced by injection moulding where at the entrance to the mould, a "gate" is present⁹).

The explanation of these results can only be given in a qualitative way. It would appear that, in both cases, the polymer has been badly mauled before entering the capillary proper. As a result, its viscosity just inside the entrance is lower than it would otherwise have been. Qualitative support for this view is to be found in the widely experienced observation that after steady shearing at a high shear rate, e.g. with a cone-and-plate apparatus, the viscosity at a lower shear rate is initially lower than the equilibrium viscosity for that shear rate.

5.3.3 The Equilibrium Quantity $n_{11} - n_{33}$

Temperature Superposition: Figure 5.17 shows results of measurements on Styron 666 of the average birefringence $\phi = \langle n_{11} - n_{33} \rangle$ at various temperatures between 130 °C and 220 °C in the reduced output range $D_s = 0.3$ to 10 s^{-1} . By shifting along the shear rate or D_s axis with a factor a_T , the measured curves are superimposable. The procedure of shifting along a rate axis to obtain superposition is termed time-temperature superposition, and was briefly alluded to in previous chapters. By the procedure it is possible to derive, by measuring at a different temperature, the probable behaviour of a given property in a rate region outside of the experimental window. The procedure has a strong em-

Fig. 5.17. The birefringence, ϕ , for the polystyrene Styron 666 measured with the slit apparatus for reduced outputs, D_S . The measurements were made at a distance of 35 slit depths from the entrance.

pirical basis for the linear viscoelastic region. However, for non-linear properties, although generally believed valid, there is not a great accumulation of experimental evidence to support its use. The physical root on which time-temperature superposition depends, is that all relaxation times of the flow processes in the material change with temperature by the same factor. For the linear region, the quantitative relation between the shift factor and the temperature is often of the WLF kind (Ref.³⁴) of Chapter 4). The master curves obtained by superposition for Styron 666 and for S111 with BASF 3, are shown in Figs 5.18 and 5.19, respectively. In these figures, an additional vertical shifting by ρT factors has also been carried out*.

For Styron 666, a few measurements were obtained with the same slit fed by a screw extruder. In this way, it was possible to make direct measurements at outputs up to 300 s^{-1} at 190°C , and compare these with the results deduced at 300 s^{-1} from the temperature shift method. The agreement is good. The shift

*Within experimental error the extra vertical shifting is an unnecessary refinement to obtain superposition. The procedure was carried out merely to comply with the normal methods in dynamic mechanical studies.

Fig. 5.18 Master plot showing reduction of measured birefringence (ϕ) at various temperatures to 190 °C for Styron 666.

Fig. 5.19 Master plot showing reduction of measured birefringence (ϕ) at various temperatures to 190 °C for BASF 3 and S111.

factors are collected in Fig. 5.20 for Styron 666 and Fig. 5.21 for BASF 3 and S111. In both cases, 190 °C is the base temperature. The shifts found from measurements of G' and G'' as a function of ω and T are also shown. It is clear

Styron 666

Fig. 5.20 Temperature shift factors obtained for polystyrene from measurements of the streaming birefringence in a cone-and-plate, in a slit die and from dynamic mechanical measurements.

Fig. 5.21 See caption to Fig. 5.20.

that all the different techniques give the same results. Thus, for polystyrene we conclude that the same time-temperature superposition is valid for the linear and the non-linear regions of rheological behaviour, as well as for optical and mechanical quantities.

The procedure will have to be refined in the case of the optical measurements when the stress-optical coefficient is a function of temperature. In this event, additional vertical shifting will be needed to obtain coincidence of the mechanical and optical rate-shift factors. This was observed with the silicone oils where the shifts to obtain superposition long the rate axis, were different for the extinction angle and the birefringence. The extinction angle gave the same results as found with mechanical measurements.

One may conjecture that comparison of the optical and the mechanical shifts along the rate axes might help one to determine the temperature dependency of the stress-optical coefficient of materials such as polyethylene over a much wider range of temperatures than is possible by the usual method of stretching the crosslinked material in an inert atmosphere. The usual procedure is not suitable for many polymers owing to stability problems and the difficulty of crosslinking some polymers. In particular, temperatures of the order of 300 °C

should become accessible by the proposed method. Such measurements could be helpful in studies of the rotational isomer balance in polymeric systems.

Molecular Weight Dependency - Polystyrenes: This was generally determined with slit A at a distance $L/a = .35$ from the entrance. Both polymers of narrow molecular weight distribution (7a, S111, 5a and 6a) and commercial polymers were measured. The polymer with the highest molecular weight, 14a, was also measured, but the results could not be used as the flow was not uniform in the 3-direction. Pressures were measured simultaneously with the ram speed and the birefringence. The results have been set out in Fig. 5.22 with the birefringence as a function of the shear stress at the wall of the slit. The quantity $\langle n_{11} - n_{33} \rangle$ is seen to vary approximately as the square of the shear stress (drawn lines), except at the highest shear stresses where in one case (S111) there is a clear tendency for the birefringence to increase at a faster rate. The reason for this is unknown, but it is noted that indications of similar behaviour have been found with normal stresses $p_{11} - p_{22}$ and polystyrene solutions at lower shear stresses than the present²⁰.

Fig. 5.22 The measured birefringence in the 1-3 plane as a function of shear stress τ_w with the slit apparatus: polystyrenes of narrow molecular weight distribution. At high molecular weights the birefringence is nearly independent of the molecular weight.

The ratio $\langle n_{11} - n_{33} \rangle / p_{12}^2$ seems to increase with molecular weight up to a critical molecular weight above which it remains constant. These results closely follow results with J_{e0} , as seen in Fig. 5.14. In analogy with the relation

of J_{e0} to the normal stress differences we define an optical quantity G_{e0} which is equal to the ratio $\frac{1}{2}(n_{11} - n_{33})/n_{12}^2$. In the limit of zero shearing, this should be equal to J_{e0} , according to the basic molecular theories (Rouse, etc.) since for these $n_{22} = n_{33}$. In the extended model, described in Section 4.3, G_{e0} should be up to 15 % smaller than J_{e0} . Indeed, it was always found that G_{e0} was smaller than J_{e0} , the average difference being about 15 % of J_{e0} . The precision of the method is, however, not sufficient for a more quantitative comparison with the theory outlined in that section. The value of $n_{22} - n_{33}$ depends on the difference between two quantities, the absolute precision of each is not better than 10 %.

The basic molecular models appear to be unsatisfactory in not giving the correct dependence of J_{e0} and G_{e0} upon the molecular weight. However, they additionally suggest that J_{e0} and G_{e0} should be sensitive to the broadness of the molecular weight distribution. The broader the molecular weight distribution, the larger the value of each quantity. In Fig. 5.23 the measured values of $\langle n_{11} - n_{33} \rangle$ are given for BASF 3, Styron 678 and S111. The commercial polymers, which have much wider molecular weight distributions than S111, show distinctly greater effects than S111. BASF 3, at equal shear stress, produces six times the birefringence which S111 gives. This is less than that would be expected on the basis of the polydispersity factor of the Rouse theory (about 9). However, it is greater than indicated in one model of Graessly (end Section 4.4) where optical strengths of these two materials should be proportional to M_z/M_w and accordingly (see Table 3.2), BASF 3 should have been only about three times stronger than S111. Similarly, the optical strength of Styron 678 seems to lie between the two models.

Fig. 5.23 The measured birefringence in the 1-3 plane as a function of shear stress τ_w with the slit apparatus: S111 and two commercial polystyrenes. At low shear stresses, the differing polydispersities determine the birefringence level.

5.3.4 Measurements in the 1-2 Plane

The experimental procedure was outlined in Section 2.2. The method should be used only when other methods of obtaining the stress-optical coefficient fail. This may occur when the material is either too viscous or too unstable (thermally). The coefficient is evaluated from the initial slope of the birefringence - shear stress relation. The birefringence, Δn , is given as:

$$\Delta n = (4 n_{12}^2 + (n_{11} - n_{22})^2)^{\frac{1}{2}} \quad (5.3.1)$$

Assuming that the stress-optical relation holds and relation (4.1.17) is valid there follows:

$$\Delta n = 2 C p_{12} (1 + (\frac{n_{11} - n_{22}}{2 n_{12}})^2)^{\frac{1}{2}} \quad (5.3.2)$$

At low shear rates $\frac{1}{2}(n_{11} - n_{22}) = J_{eo} n_{12}^2$. Substitution of this relation and expansion leads to:

$$\Delta n = 2 C p_{12} + C^3 J_{eo}^2 p_{12}^3 + \dots \quad (5.3.3)$$

The experimental results are to be fitted by a least squares procedure to a cubic polynomial of the form $A p_{12} + B p_{12}^3$. (In general, Δn is an odd function of p_{12} .) The numerical values of A and B yield the stress-optical coefficient, C, and J_{eo} .

Figure 5.24 shows the results of measurements on Styron 666 at 190 °C. The drawn curve follows the computed cubic. The dashed line has slope A and therefore represents the shear component of the total birefringence. The difference between the dashed and the full line represents the contribution from the second term in (5.3.3). The value found for C was $3.8 \times 10^{-9} \text{ m}^2/\text{N}$ compared with $4.1 \times 10^{-9} \text{ m}^2/\text{N}$ from the more accurate cone-and-plate measurements. J_{eo} was found to be 0.7×10^4 compared with 1×10^4 from the cone-and-plate measurements. It is seen that both quantities are of the correct order, the error in C being about 10 %. The results were also evaluated with an added term proportional to p_{12}^5 . The stress-optical coefficient then decreased to $3.5 \times 10^{-9} \text{ m}^2/\text{N}$, and J_{eo} increased to 1×10^4 .

Figure 5.25 shows the results of similar measurements on Solvic 229, a rigid PVC, at 210 °C. The initial slope gave a C value of $4.2 \times 10^{-10} \text{ m}^2/\text{N}$ from the cubic, and $3.8 \times 10^{-10} \text{ m}^2/\text{N}$ from the pentic polynomial, respectively.

Fig. 5.24 Path difference, by counting isochromes in 1-2 plane, as a function of shear stress for a slit of section 10 mm $\times$ 1 mm. The material is polystyrene. The dashed line determined by regression gives the initial slope and the stress-optical coefficient.

Fig. 5.25 See caption to 5.24. The material is rigid PVC.

The table below gives values of the stress-optical coefficient found by the slit method (cubic polynomial) in the temperature range 180 °C to 210 °C.

Table 5.2

Stress-Optical Coefficients of Rigid PVC

Temp. (°C)	C (m ² /N)
180	4.3×10^{-10}
192	5.5
205	5.3
210	4.2

Considering that determination of C by this method for the polystyrene led to too small a value, it is expected that the real stress-optical coefficient of rigid PVC is little higher than the values given in the table.

It is seen that the stress-optical coefficient is approximately independent of the temperature in the range considered. This is of interest since rigid PVC is believed to undergo in this temperature region, a change in its flow

mechanism from particulate or supramolecular to molecular*. The values found for C in the above, are somewhat higher than values in the literature²¹⁾ (3 to $4 \times 10^{-10} \text{ m}^2/\text{N}$). However, the latter were obtained from creep measurements extrapolated to the region of steady flow at temperatures of the order of T_g ($\sim 70^\circ\text{C}$).

5.4 Results with the Capillary Apparatus ($n_{22} - n_{33}$)

5.4.1 The Influence of Entrance and Exit Effects

Figures 5.26 and 5.27 show the basic experimental results obtained with capillary instruments on the silicone, Siloprene RS, and on the low density polyethylene, IUPAC A, respectively. In both cases the measured optical effect, proportional to $n_{33} - n_{22}$, was positive. This was seen from the position of the compensator and of the extinction fringe.

Fig. 5.26 The measured path difference in the 2-3 plane at the wall for a silicone oil as a function of the shear gradient for various capillaries and a slit with lengths, L , indicated.

*In our case, the particles must have been smaller than the wavelength of light since optical measurements were possible. It is not possible to satisfactorily measure PVC melts at lower temperatures on account of the strong depolarization that occurs (particle flow?).

The silicone oil is an optically weak material (see Table 5.1) and could not be measured with the shortest capillary. Instead, an additional measurement was made with a slit, lent by W. Philippoff. An attachment was fitted to the apparatus of Fig. 2.9. With this arrangement, the field of view was different to that in Fig. 2.9 bottom. On onset of flow with the polaroids crossed at 45 °C to the axes of flow symmetry, the central region of the split remained

Fig. 5.27 The measured path difference in the 2-3 plane for a low density polyethylene as function of shear rate for different capillary lengths.

dark, and the region near the wall lighted up. On compensation, a dark fringe moved from the central region to the wall. Compensation was taken when the fringe was judged to be at the wall. The obtained path differences at the wall were then correlated with the reduced output, D , for the slit. The gradient at the wall was obtained from D with the help of Rabinowitsch correction factors from previous calibrations of the material. For the silicone under discussion, the corrections are very nearly the same (within 10 %) for both slits and capillaries. It is therefore justifiable to compare results as a function of reduced outputs for slits and capillaries in the same figure as is done in Figs 5.27 and 5.28. The latter shows the dependency on the capillary length.

Clearly, the optical path difference increases essentially linearly with the capillary length. This indicates that the measured effect is either a real material effect indicative of non-zero $n_{22} - n_{33}$ and/or a window effect. If the whole effect were determined by the entrance flow, then one could not expect the path difference to depend on the capillary length. In the case of silicone oil, the lines, extrapolated to zero capillary length, go within experimental uncertainty through the origin of the coordinate system. For this material one concludes that, within experimental error, the optical effect is entirely due to the flow in the capillaries, and entrance or exit flows make no important contribution. In the case of low density polyethylene (IUPAC A) (Fig. 5.29) on the other hand, the linear plot extrapolated through the experimental results, indicates the existence of an entrance correction which is, however, negative. In this case, the optical effect is partially caused by entrance-exit flows. However, the entrance flow apparently compensates for the orientation formed in the capillary. Again the greatest part of the measured effect must be ascribed to

Fig. 5.28 Data from Fig. 5.26, replotted to show that the measured effect in the 2-3 plane is proportional to the capillary length and that entrance/exit effects are negligible. The reduced outputs, D , are indicated.

flow in the capillary.

Similar measurements have also been made for the polystyrene Styron 678 and BASF 3 (not shown). Again, for these materials, the optical effect varies essentially linearly with the capillary length, and entrance-exit effects were insignificantly small compared with the capillary effect. For these polystyrenes the sign of the effect was reversed, i.e. $n_{22} - n_{33}$ was found to be positive. This is in keeping with the principal anisotropies of polystyrene for which $n_{11} - n_{22}$ is negative. So, for the polystyrenes the ratio $(n_{22} - n_{33}) / (n_{11} - n_{22})$ is also a negative quantity, just as with the silicone oil and the low density polyethylene.

A remarkable result of the present findings is that the optical effect is a linear function of the capillary length. This might not have been expected after the results for the corresponding quantity $n_{11} - n_{33}$ (Section 5.3.2). The explanation is, presumably, the fact that $n_{11} - n_{33}$ may contain effects of longitudinal gradients which are optically ineffective in the 2-3 plane.

LDPE IUPAC A
 $T = 190^{\circ}\text{C}$

Fig. 5.29 Data from Fig. 5.27, replotted to show that the measured effect in the 2-3 plane is proportional to the capillary length. A small entrance/exit effect is present in this case.

5.4.2 The Influence of the Window Strain

One expects the window strain to be a function of the hydrostatic pressure on the windows and hence, on account of this alone, one might expect the optical effect to increase linearly with the capillary length. Fortunately, window strain can be discounted as being of serious importance for the results on account of the following:

- 1) By compensation with the slit measurements (silicone only), a dark fringe moved parallel to the centre line of flow symmetry towards the wall. The symmetry of the windows is cylindrical. If window strain were serious one would expect with the slit the image in the microscope to be the same as in Fig. 2.9 under. This was not observed.
- 2) The window strain was measured by blocking the exit and measuring without flow the birefringence of the windows as a function of the superimposed pressure. The effect due to the window strain was small, giving about 3×10^{-6} cm path difference at a pressure of 200 bar on both windows (see

Fig. 2.9), and gave a negative apparent birefringence. During flow, pressure is only exerted on one window. The other, opposite the exit of the capillary, is not subject to such high pressures. The highest pressures obtained with the experiments on the silicone were of the order of 70 bar. One may therefore estimate a correction of 5×10^{-7} cm, at most, to a measured effect of about 90×10^{-7} cm path difference. Owing to window strain in this case, the real optical effect should be about 5 % higher than the measured effect. This has not been taken into account in the further evaluation of the results owing to the fact that for the one material where it might be important; the error remains acceptable. For the other melts, the problem is completely absent as they are 10 to 30 times more optically sensitive than the silicone oil and possible corrections for window strain lie well within the experimental error.

5.4.3 Comparison of $n_{22} - n_{33}$ with $n_{11} - n_{22}$ and $n_{11} - n_{33}$

In Fig. 5.30, for Siloprene RS at room temperature, the obtained values of $(n_{33} - n_{22})$ are set out against the shear gradients at the wall of the die. The same figure includes results of $n_{11} - n_{22}$ and Δn measurements with the cone-and-plate apparatus and a concentric cylinder apparatus. It is seen that $n_{33} - n_{22}$ is about 10 % of $n_{11} - n_{22}$. Strangely, $n_{33} - n_{22}$ seems to lie more parallel to Δn than to $n_{11} - n_{22}$. However, the effect is partly illusory, and with increasing q the ratio of $n_{33} - n_{22}$ to $n_{11} - n_{22}$ does not decrease greatly.

Fig. 5.30 Various birefringences plotted as a function of the shear rate, q , for a silicone oil. $\nabla \dots \Delta n$ (concentric cylinder); $\nabla \dots \nabla n$ (cone-and-plate); $\blacksquare \dots n_{11} - n_{22}$ (cone-and-plate); $\circ \blacksquare \dots n_{33} - n_{22}$ (capillaries).

In Fig. 5.31 the obtained values of $n_{33} - n_{22}$ for LDPE, IUPAC A at 190 °C, are plotted against the calculated gradients at the wall of the die. Also included in this figure are measurements of $n_{11} - n_{22}$ and Δn obtained with the cone-and-plate apparatus, and $n_{11} - n_{33}$ obtained with the slit apparatus. The cone-and-plate measurements were carried out at 150 °C and transposed to 190 °C by temperature shifting. (The particular low density polyethylene was not thermally very stable.) The unfilled squares represent extrapolated equi-

librium values of $(n_{11} - n_{22})$ with the cone-and-plate and are seen to agree very well with the $(n_{11} - n_{33})$ measurements with the slits.

Fig. 5.31

Comprehensive plots showing the gradient dependency of the various deviatoric combinations as determined by various apparatuses. Fig. 5.31 ... polyethylene low density; $\bullet$... Δn (cone-and-plate); $\blacksquare$... $n_{11} - n_{22}$ (cone-and-plate); $\blacktriangledown$... $n_{11} - n_{33}$ (slits); $\bullet$ $\blacktriangledown$... $n_{33} - n_{22}$ (capillaries) Fig. 5.32 ... polystyrene.

Fig. 5.32

In Fig. 5.31 there is an apparent discontinuity at about 1 s^{-1} , which marks the onset of overshoot phenomenon with the cone-and-plate measurements. True equilibrium was not attainable within experimental time available just in the shear rate region where overshoot, and possible structural breakdown, first occur. At high shear rates in the overshoot region, equilibrium is obtained after a few minutes. As the shear rate is decreased, the equilibrium time strongly increases (becomes hours), and it is no longer possible to make a satisfactory extrapolation to steady flow conditions: measurements are again "constant" after about five minutes. This difficulty often occurs with low density polyethylenes. Apart from this blemish $n_{33} - n_{22}$ is seen to be about 10 % of $n_{11} - n_{22}$ and $n_{11} - n_{33}$.

Figure 5.32 gives the results for Styron 678 at 190°C . Again $n_{11} - n_{22}$, Δn , $n_{11} - n_{33}$ and $n_{33} - n_{22}$ are plotted against the gradient. Only the overlap region is shown; results for higher gradients with the slit and lower gradients with the cone-and-plate have been left out.

All the results concerning the $n_{22} - n_{33}$ effect have been collected and re-plotted in the following figure (Fig. 5.33) to show the ratio $(n_{33} - n_{22}) / (n_{11} - n_{22})$ as a function of the shear gradient.

A few results, obtained by Philippoff (23 % PIB in oil) using the same method are also shown. The value of the ratio 0.05 to 0.14 is of the order found with the most reliable normal stress measurements²³). A few results with the narrow molecular weight polystyrene, S111, were determined by using the

Fig. 5.33 Plot of ratio $(n_{33} - n_{22})/(n_{11} - n_{22})$ for various melts. Data on a polyisobutylene melt (Oppanol B5) and a solution from Ref. 22) are also shown. • ... Styron 678; •... BASF 3; ■... Silopren RS; ▽... IUPAC A; ○... Oppanol B5; ○... 23 % PIB in oil.

indirect method of Section 5.3.3. These are also in agreement (ratio was about 0.08) with the results in Fig. 5.33.

Remarkable is the constancy of the ratio for the polystyrenes and also for the low density polyethylene; both materials were in their non-Newtonian regions of flow.

The silicone oil and the polyisobutylenes tend to show a monotonic decrease in the ratio, as the shear rate is increased. However, the decrease is not considerable. Theoretically, we might expect the ratio not to be altered by an initial departure from second order flow (this can be proven for rigid particles of ellipsoidal shape). Ultimately, we expect the ratio to decrease to zero since in the case of extreme chain stretching the cross-section along the axial coordinate should become circularly isotropic. An attempt has been made to check this by examining sections of injection moulded polystyrene (see also Sections 5.1.3 and 5.5.2). Astonishingly, $n_{33} - n_{22}$ at the peaks (e.g. Fig. 5.9) was still about 10 % of $n_{11} - n_{33}$ ($\approx \Delta n$), even under these extreme conditions. This particular experiment may not have been very meaningful because of the complicated stress pattern in injection moulding. Nevertheless, it remains an interesting point. There is no easy way of doing the same for the silicone oil.

5.5 Applications

5.5.1 The Relations between Steady Shearing Flow and Oscillatory Shearing

Cox and Merz²⁴⁾ discovered a relation between the viscosity in steady shearing flow and the absolute value of the dynamic viscosity. The relation is expressed:

$$\eta(q) = |\eta^*(\omega)| \quad ; \quad \omega = q \quad (5.5.1)$$

Probably, this result is only valid for polymer melts and for these systems it has been well established²⁵⁾²⁶⁾. A theoretical foundation for (5.5.1), either from molecular or from phenomenological theories of non-linear behaviour, has not yet been found.

As regards theories that compare high shear rate behaviour in steady flow with dynamic behaviour of polymeric systems, two types exist. The first group of theories assumes that the material is essentially unchanged during flow so that a suitable equation of state will describe both linear viscoelastic behaviour and flow at high shear rates. This was done by a number of authors: Bueche²⁷⁾; Roscoe²⁸⁾; Pao²⁹⁾; Zapas³⁰⁾. The second group of theories uses the assumption that the material changes during the steady flow because a structure (e.g. entanglements) is broken down: Yamamoto³¹⁾; Graessly³²⁾; Schroff³³⁾; Booi³⁴⁾.

Roscoe obtained:

$$\eta(q) = \eta'(\omega) \quad ; \quad \omega = mq \quad (5.5.2)$$

$$(p_{11} - p_{22})/(2q^2) = G'(\omega)/\omega^2 \quad ; \quad \omega = mq \quad (5.5.3)$$

$$\frac{1}{r+1} \left(\frac{p_{11} - p_{33}}{q^2} \right) = G'(\omega)/\omega^2 \quad ; \quad \omega = mq \quad (5.5.4)$$

where m and r are material constants. In view of the experimentally found result that $p_{11} - p_{33}$ is close to $p_{11} - p_{22}$ for all the materials of this investigation r may be set equal to unity.

One can summarize the above system of equations by saying that the theory predicts a constant shift m along the logarithmic rate axis for superposition of steady flow and linear dynamic-mechanical quantities. The shift factors for the normal stress coefficients and the viscosity should be the same. A constant shift along the rate axis is not consistent with equation 5.5.1 nor with experiment. To a fair approximation, however, the experimental results are often consistent with the following empirical relationship²⁶⁾.

$$\eta(q) = |\eta^*(\omega)| = \eta' \left(\frac{\omega}{m} \right) \quad m = m(\omega) > 1 \quad (5.5.5)$$

$$\frac{1}{2} \left(\frac{p_{11} - p_{22}}{q^2} \right) \approx \frac{1}{2} \left(\frac{p_{11} - p_{33}}{q^2} \right) = G' \left(\frac{\omega}{m} \right) \left(\frac{m}{\omega} \right)^2 \quad (5.5.6)$$

Typical of the second group of theories is the theory of Schroff. This may be cast in the form:

$$\eta(q) = \int_{-\infty}^{\infty} H(\tau) K(\tau q) \tau d \ln \tau \quad (5.5.7)$$

This is an integral equation for the steady shearing viscosity. The kernel $K(\theta)$ with $\theta = \tau q$ is in this theory given by the functions h and g of Graessly: $K(\theta) = h(\theta)g(\theta)^{3/2}$. The theory of Booi can also be cast in the form of equation (5.5.7). In this case the kernel is equal to unity for q less than b and to

zero for q greater than b (see Section 4.5).

Some of the theories of the first group can also be cast in this general form. In, for example, that of Roscoe and in a simplified version of the Kaye-Bernstein-Kearsley-Zapas theory³⁵⁾ where the kernel has the form:

$$K(\theta) = (1 + 2\theta^2/9)^{-1} \quad , \quad \theta = \tau q$$

By curve fitting it is always possible to find a kernel which will fit given experimental results either for the viscosity or for the normal stress function. The question arises: is it possible to use the same kernel for the normal stresses and the viscosity, and can the same kernel be used for different polymeric systems. For the normal stresses the relation should read:

$$\frac{1}{2} \left(\frac{P_{11} - P_{22}}{q^2} \right) = \int_{-\infty}^{\infty} H(\tau) K(\tau q) \tau^2 d \ln \tau \quad (5.5.8)$$

For polymer solutions the problem has already been examined by Tanner³⁶⁾. He concluded from examination of available literature that this was not possible in general. The kernel from the viscosity curves causes appreciable error in predicting normal stresses. However, smaller errors in predicting viscosities were found if the kernel was obtained from the normal stress data. His method of tackling the problem was to use the experimental data and treat (5.5.7) and (5.5.8) as Fredholm equations and find F by iterative means. This is somewhat unsatisfactory as $H(\tau)$ needs to be found by a separate inversion of linear viscoelastic data and the experimental region is often restricted. It will be recalled that, in principle, inversion is only possible if one knows the behaviour over the entire frequency range zero to infinity. These problems may be overcome by finding a linear combination of $\eta'(\omega)$ and $\eta''(\omega)$, which agrees with the viscosity in steady shear over the experimental range (up to five decades in rate). For the polystyrenes S111, BASF 3, Styron 678 and Styron 666, the same relation was found to hold for the viscosity:

$$\eta(q) = \eta'(\omega) + \frac{1}{3} \eta''\left(\frac{\omega}{2.5}\right) \quad , \quad \omega = q \quad (5.5.9)$$

This experimental relation is just as good as the relation of Cox and Merz. The experimental support for this contention is plotted in Figs 5.34 to 5.36. The advantage of (5.5.9) over the Cox and Merz relation is that it is linear. After considering the integral forms for $\eta'(\omega)$ and $\eta''(\omega)$ - see equations (1.2.7) through (1.2.10) - the kernel follows immediately:

$$K(\theta) = \frac{1}{1 + \theta^2} + \frac{1}{3} \frac{(\theta/2.5)}{1 + (\theta/2.5)^2} \quad , \quad \theta = \tau q \quad (5.5.10)$$

Fig. 5.34 Comparison of steady flow viscosity with dynamic viscosities:
 $\circ \dots \eta(q)$; $\odot \dots$ relation (5.5.9); $\Delta \dots \eta'(\omega)$; $\circ \dots \eta''(\omega)$.

Fig. 5.35 Comparison of steady flow viscosity with dynamic viscosities:
 $\circ \dots \eta(q)$; $\odot \dots$ relation (5.5.9); $\Delta \dots \eta'(\omega)$; $\circ \dots \eta''(\omega)$.

The normal stress coefficients as obtained from birefringence measurements, were difficult to fit. Just as with the viscosities, there are many ways of obtaining superposition. The best one found is indicated by the following equation:

$$\frac{(P_{11} - P_{22})}{2q^2} = \frac{G'(\omega)}{\omega^2} + \lambda\{\eta_0 - \eta'(\omega/2.5)\}/\{\omega/2.5\}, \quad \omega = q \quad (5.5.11)$$

The above relation gives a kernel of the same form as the kernel for the steady flow viscosity, but the factor 1/3 in (5.5.9) is replaced by a parameter λ . The kernel becomes

$$K(\theta) = \frac{1}{1 + \theta^2} + \lambda \frac{(\theta/2.5)}{1 + (\theta/2.5)^2}, \quad \theta = q\tau \quad (5.5.12)$$

The values of λ were 1/4 for S111, 1/30 for BASF 3 and 1/20 for Styron 678. Resulting fits of the normal stress coefficients to the dynamic-mechanical quantities via (5.5.12) are shown in Figs 5.37 to 5.39. The normal stress coefficients were obtained in the lower shear rate range with the cone-and-plate apparatus and in the high shear rate range with the slit apparatus.

Fig. 5.36 Comparison of steady flow viscosity with dynamic viscosities: $\bullet \dots \eta(q)$; $\blacktriangle \dots \eta(\omega)$; $\circ \dots \eta''(\omega)$; the drawn line is relation 5.5.9.

Fig. 5.37. Comparison of steady flow elastic properties with dynamic data: $\blacktriangle \dots \frac{1}{2}(p_{11} - p_{22})/q^2$; $\circ \dots G'(\omega)/\omega^2$; $\square \dots$ relation (5.5.11); $\Delta \dots$ from relation (5.5.10).

Fig. 5.38 Comparison of steady flow elastic properties with dynamic data: ▲ ... $\frac{1}{2}(p_{11} - p_{33})/q^2$ (slit); ○ ... $G'(\omega)/\omega^2$; □ ... relation (5.5.11).

Fig. 5.39 Comparison of steady flow elastic properties with dynamic data: ▲ ... $\frac{1}{2}(p_{11} - p_{22})/q^2$; ○ ... $G'(\omega)/\omega^2$; □ ... relation (5.5.11).

In the latter case, experimental data were all increased by 10 % to eliminate the slight difference between $n_{11} - n_{33}$ and $n_{11} - n_{22}$. In one figure, normal stress coefficients have also been predicted from the kernel for the viscosity function, i.e. by using $1/3$ instead of $1/20$ for Styron 678. The prediction was poor and can be seen in Fig. 5.37. The reverse procedure was also tried, i.e. trying to fit viscosity data with the kernel from the normal stresses. This was just as unsuccessful. Similar results were also found for the other commercial polystyrenes. We can conclude that it is not generally possible to interchange the normal stress and the viscosity kernels.

However, for S111 which has a narrow distribution of molecular weights, the kernels for the viscosity and the normal stresses are very nearly equal.

Schroff³³⁾ used a kernel from the theory of Graessly to calculate the steady shear viscosity from the spectrum of relaxation times $H(\tau)^*$. The materials he examined, were high-density polyethylene melts, and the kernel he used, showed a much sharper cut-off than the kernels found here. Computer calculations with his kernel and the spectrum $H(\tau)$ evaluated from dynamic moduli measurements, failed to reproduce the steady flow curves shown here for S111. At the highest shear rates the calculated viscosity was too low by a factor four and the normal stress coefficient by a factor of twenty. Other theoretically based kernels

*It is not sure that the proposal of Schroff is consistent with the ideas propounded by Graessly.

have been investigated as well. One was $\sin^{-1}(q_T)/q_T$ which has been proposed on the basis of the Ree-Ehring theory for non-Newtonian flow³⁷⁾. This was also inadequate: at the highest shear rates, the viscosity was a factor three too high and the normal stress coefficient a factor twenty too high.

Other systems have also been investigated, but the results were not so conclusive. Measurements on the low density polyethylenes LDND and LDBD (see Table 3.1) showed in a IUPAC Working Party investigation that the zero shearing viscosity did not agree with the real part of the dynamic viscosity at low frequencies⁶⁾. This discrepancy has also been found on occasions by other workers with low density polyethylenes. On account of this difficulty and the problem that equilibrium measurements of $n_{11} - n_{33}$ are for practical purposes non-existent for these materials (see Section 5.3.2), at very high shear rates, further investigation of the kernel approach seemed of limited value.

5.5.2 The Orientation in Injection Moulding

The control of product anisotropy can be of importance to the producer, since some important properties of the finished product are sensitive to the degree of orientation present. Thus, it is known that impact strength and environmental stress resistance are considerably affected by the degree of molecular orientation determined by birefringence. In conjunction with J. van Leeuwen and R. van der Vijgh, the present author has shown⁹⁾ that, in the case of moulded strips (see Section 5.1.3), the peak orientation in the strip is related to the orientation in steady, isothermal, flow.

The basis of this investigation is the result mentioned in 5.1.4, that the birefringence induced in polystyrene by steady flow, is governed by the shear stress, regardless of temperature. This prompted the suggestion that, for molecular orientation occurring during the non-isothermal cavity filling process, the shear stress might be an appropriate and exclusive variable provided relaxation of the orientation which is temperature dependent, does not get the chance to disturb the situation appreciably.

The slit apparatus is appropriate to characterize steady, isothermal flow orientation. In fact, only with this apparatus is it possible to measure at the high shear stresses which occur during injection moulding.

The materials were a straight polystyrene (Styrene 678), a rubber modified polystyrene (Styrene 475) and an acrylonitrile-butadiene-styrene copolymer (ABS). The latter compounds were only translucent in thicknesses of less than one millimeter. This was sufficient, however, for measurements in the 1-3 plane. Owing to the depolarizing effects of the rubber particles, birefringence measurements could not be carried out in the other two planes. With the slit apparatus both these compounds showed the same qualitative behaviour as the straight polystyrene, i.e. the birefringence was essentially a function of the shear stress only.

Figures 5.40 and 5.41 show results of the tests in steady, isothermal flow with these compounds. These results are interesting in that the stress-optical relation is not expected to hold for these two phase materials. The reason for the simple behaviour may lie in the probable fact that only the polystyrene phase is considerably deformed during melt flow and that the stress-optical

coefficient of the polystyrene phase is predominant.

Fig. 5.40 Styron 475.

Fig. 5.41 ABS (ref.⁹)).

Flow birefringence in 1-3 plane for steady isothermal flow. A simple relation between the orientation and the shear stress is retained at all temperatures, even for these two-phase materials.

The orientation formed during the filling process and frozen in the injection mouldings, show a complicated pattern. Simplest is to view the whole plates in a perpendicular direction between crossed polaroids, and to count isochromes in order to obtain the longitudinal distribution of birefringence in the 1-3 plane. Figure 5.42 shows an example of this for Styron 678 at various moulding conditions. Typically, one finds a peak or plateau near the gate, whilst at the frozen flow front there is no optical effect.

For the interpretation of the results, only the peak value of the birefringence in the 1-3 plane was used. This was directly compared to the equilibrium birefringence in steady, isothermal flow. The parameter of comparison being the shear stress. The shear stress in the mould was defined by the average slope of the pressure distribution in the mould just before the hydraulic pressure was shut-off. Two types of moulding conditions can occur:

- a) Short - the mould is just filled or incompletely filled. The melt-entry pressure is then a direct measure for the shear stress.
- b) Flash - the mould is overfilled and the melt-entry pressure gives an over-estimation for the shear stress in the mould.

Both of the above conditions were examined with two moulds. The first, of the butterfly type, had relatively short and loss-free runners (runners are the channels through which the melt flows before reaching the cavity). The cavity of this mould had dimensions $1 \times 65 \times 65 \text{ mm}^3$. With this mould it was

Fig. 5.42 Typical examples of the birefringence in the 1-3 plane in injection moulded plates of straight polystyrene Styron 678. Open symbols ... short condition; filled symbols ... just flash condition.

only possible to measure the melt entry pressure and not the pressure distribution in the mould. The rubber modified polystyrene and the ABS were measured with this mould in a study of the influence of moulding conditions on orientation and product properties⁹⁾. The cavity of the second mould had dimensions $2 \times 65 \times 300 \text{ mm}^3$. With this mould the pressure distribution could be measured for a wide range of conditions using the straight polystyrene. Figures 5.43 through 5.45 show plots of the peak values of $n_{11} - n_{33}$ in the 1-3 plane as a function of the shear stress at the wall at the end of the cavity filling process for rubber modified polystyrene and straight polystyrene, respectively. Comparison with the isothermal data, as represented by the drawn lines, shows good agreement for all short data although the scatter is considerable. The flash data for the rubber modified polystyrene and the ABS deviate in a direction to be expected from an overestimation of the shear stress in the mould.

In spite of the difficulties for a detailed interpretation of all observations, the fact remains that the birefringence in injection moulded objects can be explained and predicted semiquantitatively from the flow birefringence in steady shear flow. Other mould geometries, where radial flow plays an important role, may give different details. There is no doubt, however, that they will show similar general features.

Fig. 5.43

Fig. 5.44

The maximum birefringence in the 1-3 plane of mouldings as a function of the shear stress at the cavity wall for the short and the flash conditions. The drawn line represents isothermal, equilibrium, flow conditions. With the mould used, the shear stress is overestimated under flash conditions.

Fig. 5.45 Straight polystyrene Styron 678. See captions to Figs 5.43 and 5.44. With this mould the shear stress should be estimated equally well for both flash and the short conditions.

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6. Discussion

6.1 The Stress-Optical Relation

In the preceding sections we have shown that the stress-optical law holds for amorphous melts during steady shear flow. The simple stress-optical law is remarkable in that it bridges the macroscopic stress with the microscopic inner processes, i.e. the rotations and deformations of the atomic bondings. Remarkable too, because relations between the stresses and strains or strain rates are non-simple, and not usually of general applicability. In fact, in the world of mechanics, the molecular theory of the stress-optical relation in polymers gives the only theoretical relation between measurable quantities which actually works over a wide range of conditions and variables. To exemplify this remark we recall that the stress-strain relations for rubbers are not understood since the ad hoc C_2 term of Mooney-Rivlin has to be added in order to achieve curve fitting. The value of C_2 is not even constant but changes for a given material when the type of deformation is changed: C_2 is smaller in simple shear than in uniaxial extension¹⁾. The situation is even more complicated for solutions and melts since it can still be safely said that non-Newtonian flow is not fully understood. Yet, for both solutions and melts, when one takes the simplest theory, eliminates the strain rate from the stress-strain rate and strain rate-birefringence relations, one obtains the same simple relation between the stresses and the birefringence which is obtained for rubbers by eliminating the strain from the stress-strain and strain-birefringence relations. The proportionality factor is typical for a given polymer type independent of whether the polymer has been crosslinked, diluted or left undiluted, has low or high molecular weight, has a broad or a narrow molecular weight distribution or is being sheared or uniaxially stretched at low or high deformations.

The reason for the success of the stress-optical relation and the relative lack of success of relations between strain rates or strains and the stresses or birefringence is not sure. It must be admitted that a chance compensation may have taken place between factors not taken into account by the simpler molecular theory. The factors we have in mind are the internal field on the one hand and the crowding problem for chain statistics on the other. The first involves the Lorenz-Lorentz field which must be too crude when the system becomes deformed.

Orientation of the chains, effects the internal field in two ways: through the intra-molecular orientation and through the inter-molecular orientation. The intra-molecular effect is always present, but the inter-molecular effect, depending on the changing distance between the chains, should be reduced by the addition of solvent, because at high dilutions the chains are so far apart that small relative changes in inter-chain distances have no appreciable effect.

Legrand²⁾ has made a start on this particular problem by treating the case of simple extension. More general results are not available. According to Legrand, a careful account of the influence of deformation on the internal field should also account for the C_2 term in rubber elasticity since the van der Waals

binding forces are also determined local dipole interactions. It is supposed that the intermolecular cause will be the dominant factor for the determination of C_2 .

The second factor referred to in the above has been taken into account by Jackson and co-authors³⁾. These authors point out that the Gaussian or random walk model for chain statistics is based on assumptions that the medium in which the chain acts, is isotropic in action. This is clearly an unreasonable assumption for an undiluted system, because when the individual chains are deformed, the medium becomes anisotropic. Chain steps should not be equally probable in all directions. To be properly self-consistent, the model should take this bias into account. The afore-mentioned authors did this for simple extension and obtained the right kind of behaviour for elastomers.

Since both of these theoretical possibilities have the same qualitative effect, it is just possible that their combination will still lead to the same, simple, stress-optical relations, as discussed earlier. If this speculation is true, we should then only speak of a quasi-linearity in the relations between the stresses and the birefringences.

For another class of amorphous materials - filled systems - we do not expect the stress-optical relation to hold, except for very special cases. Depolarization due to particle scattering, makes any experimental investigation with filled systems very difficult. Nevertheless, there exist a few filled systems which show but a small degree of depolarization. One such material, a clear acrylonitrile-butadiene-styrene copolymer, was presented very kindly by J. Young of Borg-Warner Chemicals. Scattering in this material has been reduced by matching the refractive index of the components. The 1-2 plane birefringence, the extinction angle χ are shown in Fig. 6.1 for this material.

Fig. 6.1 The gradient dependency of the extinction angle χ and the birefringence Δn in the 1-2 plane for a clear ABS. The stress-optical relation fails for this material. $\bullet \dots \chi$; $\circ \dots \Delta n$. The birefringence was negative for this material.

The stress-optical relation fails because, whereas the extinction angle monotonically decreases and the shear stress monotonically increases, the birefringence goes through a maximum. A similar behaviour also occurs with dilute non-matching solutions of polystyrene⁴⁾. The birefringence is then the sum of a positive form effect, and a negative "eigen" effect of the polystyrene. Both effects have differing shear rate dependencies and the sum behaviour is similar to that in the figure.

For non-steady flows, the bounds of validity of the stress-optical relation are still to be delineated. For matching solvents there is already in existence a theory^{5,6)}, which seems to be successful in describing deviations from the stress-optical law at higher frequencies⁷⁾. A phase difference between the stress and the birefringence is caused by the presence of internal friction (a force in the chain caused by the rate of relative movement between its parts, it should also be active in the absence of any surrounding medium). The same internal friction causes the viscosity η' to level-off at high frequencies to a constant value instead of steadily decreasing as in the Rouse or Zimm theory. The ratio $\eta'(\infty)/\eta'(0)$ is directly proportional to the internal friction and is a direct measure of the latter's relative importance. The introduction of internal friction might therefore be a good trick to obtain a molecular description of actual melt behaviour. It appears, however, that $\eta'(\infty)/\eta'(0)$ is so extremely small (< 0.01) for melts that internal friction can be neglected. Thus, if one uses the device of internal friction, one does not expect in the first instance any serious deviations from the stress-optical law.

Continuing with the question of non-steady flows, it may become necessary to distinguish between time-dependent motions at temperatures close to T_g and time-dependent motions at temperatures far removed from T_g . Below T_g , the birefringence is determined principally by bond deformations, whereas above T_g it is determined mainly by long-range rearrangement of the chains. Traversing T_g by decreasing the temperature, the long-range processes become frozen. According to the empirical time-temperature superposition, one can approach T_g at temperatures above T_g by increasing the time rate of a motion. Therefore, at temperatures not too far removed from T_g , we do not expect the stress-optical relation to hold for non-steady motions of the material. Polymers which probably suffer this restriction are polymethyl methacrylates, polyvinylchlorides and polystyrenes, since these are not normally examined at temperatures far removed from their glass temperature. Other polymers might not suffer this disadvantage, although, as indicated, a full investigation has not been performed. Under the aegis of a IUPAC Working Party, a few experiments have been made to examine the stress-optical rule on IUPAC A, a low density polyethylene (see Section 3)⁸⁾. The experiments were steady shearing after sudden starting of the rotor of a cone-and-plate. The optical quantities were compared with the time dependencies of the shear and the normal stresses under the same circumstances. The optical behaviour was qualitatively the same as the mechanical, but quantitative differences were present. The shear components showed good agreement as the ratio $\Delta n \sin 2\chi / 2p_{12}$ remained constant, equal to the value for steady shearing. The ratio $\Delta n \cos 2\chi / (p_{11} - p_{22})$ was too high at low shear rates and too low at high shear rates. The maximum difference was about 20 %. Definite conclusions cannot be drawn as yet from these experiments,

as there are difficulties in the measurement of the time dependency of the normal stresses with the Weissenberg apparatus. A particularly important feature is that the time dependency is a function of the angle between the cone and the plate. At short times, the overshoot increases with increasing angle until an angle of about 8° is reached where the signal becomes consistent⁸⁾. The origin of this unwished-for effect is the small displacement needed to measure the normal force. The birefringence apparatus differs in that stresses are not measured, friction is not important, and any displacement between the cone and the plate should be prevented by the thrust bearings.

The definitive experiments on this subject will have to be carried out with better apparatuses whereby, in the case of flow birefringence, the laborious compensation of the optical effect from the prism will have to be avoided. In the case of the normal stresses, the displacement problem will have to be solved as wide angle cones could lead to incorrect results on account of secondary flows or intractable boundary conditions.

6.2 The Diffusion Equation

It is worth-while spending a little time considering the diffusion equation 4.2.8. In the general form quoted, $\underline{F}$, is supposed capable of being a non-linear function of the distance between the end points of the chain. Indeed, some authors have used non-linear forms of the chain force, e.g. a Langevin function^{9,10)}. Their idea was to obtain non-linear macroscopic behaviour from the diffusion equation. The basic philosophy lies close to that in the quasi-static model for streaming flow. The forces in the chain are supposedly related to the average deformation of the chain as if the material were an elastomer and equilibrium conditions could exist. The justification for the procedure is that in the absence of flow, $\underline{V}$ is equal to zero and ψ in 4.2.8 becomes, as it must, equal to ψ_0 . There are several comments to be made at this point. The first is, that such approaches rely heavily on theoretical results for non-linear behaviour of elastomers, whilst ignoring the fact that there is as yet no conclusive evidence that such theories hold even for the systems they are intended. Secondly, there are other possible extensions to account for non-linear behaviour. For example, one could consider the term inside the inner brackets of equation 4.2.4, as the first term of a Taylor series, and simply add further terms, such as $(S - S_0)\delta(S - S_0)$ with $S=kT \text{ grad log } \psi$.

We suspect that the aforesaid approach might be incorrect, because the derivation of the Brownian motion force in the original equations was made for small deviations from equilibrium. For a proper account of non-linear effects, the writer fears that one will have to return to a basic statistical hypothesis, such as the "Master" equation of Markoff, relating the probability in momentum and configuration space to the transition probabilities*. The derivation of a diffusion equation from the "Master" equation depends on a series of linearizations in the momentum space¹¹⁾. As an example, the basic form of the Fokker-Planck equation obtained during the derivation of the Smoluchowski equation from first principles, is of the form:

*Fears, because the theory will become even more indigestible and it would seem inevitable that uncontrollable parameters will be introduced.

$$\frac{\partial \phi}{\partial t} = -a_1 \frac{\partial \phi}{\partial x} + a_2 \frac{\partial^2 \phi}{\partial x^2} \quad (6.1)$$

It contains two constants a_1 and a_2 which represent the first and second moments of the deviations (fluctuations) in the momenta. The second constant a_2 represents the diffusion constant. Higher order terms have been neglected. Owing to this latter approximation, one suspects that the diffusion equation in present use is not really suitable for the prediction of non-linear phenomena. A parallel state of affairs already exists in the theory of (Nyquist) noise in electrical circuits. These systems, apparently, are also governed by a Fokker-Planck equation. In this electrical analogy it can be proven that it is impossible to obtain the macroscopic behaviour from the (microscopic) diffusion equation by allowing in an ad hoc way, the coefficients a_1 and a_2 to be non-linear functions of the state variables¹²⁾. It is necessary to add third and higher moments of the fluctuations giving third and higher order derivatives in the diffusion equation. Whether this stringent conclusion is of serious consequence for the case in hand, is unknown since the Smoluchowski equation contains a further series of approximations¹¹⁾.

Having made these remarks, it is interesting to note that in amorphous rubbers, the diffusion of small molecules is unaffected by the degree of stretching of the matrix as long as the latter does not crystallize¹³⁾. This might be interpreted to mean that the Brownian motion of the segments in the chain is unaltered by the stretching process. If this is a correct interpretation of the findings, then it is very possible that, notwithstanding the remarks of this section, the diffusion equation as represented by 4.2.3 is still a very useful starting point and can lead to meaningful results.

6.3 The Deviatoric Components

The existence of the deviatoric combination $n_{22} - n_{33}$ has been demonstrated. The ratio of this difference to the first difference $n_{11} - n_{22}$ is of the order of magnitude expected from determinations of the first and second normal stress differences. The ease and accuracy of the optical determinations far exceeds that from stress measurements. In principal, it is possible to determine the value of $n_{22} - n_{33}$ independent of $n_{11} - n_{22}$ or $n_{11} - n_{33}$ whilst the accuracy of the second normal stress difference depends on the accuracy of the determinations of $p_{11} - p_{22}$ and $p_{11} - p_{33}$.

The value of the experimentally determined ratio $(n_{33} - n_{22})/(n_{11} - n_{22})$ was remarkably constant and always seemed to lie in the range 0.05 to 0.14. The ratio was clearly independent of the molecular weight and the molecular weight distribution of the polymer type. The above-mentioned range of experimental values for the optical ratio is, however, distinctly lower than the value derived in the model theory of Chapter four. The value obtained ($= 1/8$) in that chapter was in fact a limiting upper bound which could never be reached in practice. The reason for this is that the ratio of the principal diffusivities for rod- or ellipsoid-like particles reaches a value of two only in the case of extremely great length to diameter ratios. Significant deviations from the limiting case are still present for length to diameter ratios of one hun-

dred. The reason for this is that the limiting condition is only reached as fast as $\log (L/d)$ approaches infinity. Perhaps it would have been more physically realistic to assume that the rod had a length to diameter ratio equal to that of the random link in the theory of chain dimensions. For many polymers, the random link contains about ten C-C bonds and so to an intuitive approximation, the length to diameter ratio of the diffusion units should also be about ten to one. When this assumption is made, the optical ratio lies within the range of the experimentally found values.

The last result lends some credulity to the theory of Chapter four. Further support comes from the concentration dependence of the ratio $n_{33} - n_{22}$ to $n_{11} - n_{22}$ for a given polymer. According to the model, the ratio should be independent of the concentration of the polymer. Whilst this work has not been concerned with solutions, a few incidental measurements have been made to check the point. It was found that ten and fifteen percent solutions of BASF 3 in Aroclor at room temperature gave the same value for the ratio as the melt. Also, a four percent solution of a National Bureau of Standards polystyrene gave values for the ratio of about 0.08 which is in agreement with the results for the other polystyrenes. For these reasons, we feel that the model theory given in Chapter four gives, at least the correct physical origins of the second normal stress difference in polymers, whilst retaining the stress-optical relationship.

As a corollary for very stiff molecules, e.g. solutions of cellulosic derivatives or polar molecules in ionic solvents, we expect the ratio of the second to the first difference to be somewhat higher than the present values and nearer the limiting theoretical value. This prediction needs experimental confirmation.

The idea to use the anisotropy of diffusivity of the segments to obtain $n_{22} - n_{33}$ arose from a paper of Copic¹⁴⁾ concerning the anisotropy of diffusivity due to the working of the hydrodynamic interaction between the spheres in a dumbbell model. As he was only interested in non-Newtonian viscosity, he did not include the normal stress components in his calculations. In the limit of infinite shearing, he found the same ratio of two for the principal diffusivities. There is thus some connection with his ideas and the results presented here. The difference lies in that the present approach accounts for near neighbour interactions in the bead model, whereas his calculations were concerned with long-range interactions.

The dependency of $(n_{11} - n_{33})$ on the shear stress was found to be quadratic for several monodisperse polystyrenes and very nearly quadratic for the commercial polystyrenes. One polystyrene with a narrow distribution of molecular weight (S111) distribution showed an increased sensitivity at the very highest shear stresses, whilst another, with a lower molecular weight (Pressure Chemical No. 7a), retained even at the highest shear stresses its approximate quadratic behaviour. In the high shear-stress region, S111 shows a nearly quartic relation between $(n_{11} - n_{33})$ and the shear stress. We cannot offer any explanation for the increased sensitivity of S111. It may be remarked, however, that a similar kind of behaviour has been found for solutions of polystyrene, but again only for materials of narrow molecular weight distribution¹⁵⁾. Materials with a very broad molecular weight distribution, such as the polyethylenes of

this investigation, show a decreased sensitivity to the shear stress when one leaves the quadratic region. The constant, nearly quadratic, dependency of some polystyrenes up to the very highest shear stresses, is therefore a compensation of two different causes. Tanaka¹⁶⁾ and others have shown for a model of non-linear behaviour how the various types of behaviour could be related to the shape of the relaxation spectrum.

6.4. The Molecular Models Applied to Melts

The results of the present investigation with melts are in line with the results of other workers who used different experimental techniques. As indicated earlier, the general opinion is at present that the Rouse theory is not sufficient to describe melt behaviour, the molecular weight dependency of the compliance J_e being the great stumbling block. However, it should not be forgotten that the prediction in the theory is born out remarkably in the region of low molecular weights: quantitative agreement is obtained (see Fig. 4.1). The same results were obtained in this investigation. Additional support for the spirit of the basic molecular model, are the results for the second normal stress difference which would also seem to follow the predictions of the diffusion theory given in Chapter four. Rejection of the Rouse model applied to melts, would probably imply rejection of theory and interpretation of the results for the ratio $(n_{33} - n_{22})$ to $(n_{11} - n_{22})$. We remark at this point that we do not expect any further extension of the dumbbell model to the multi-bead case would lead to differing results for the ratio $(n_{33} - n_{22})$ to $(n_{11} - n_{22})$. This writer feels that it is still possible that the basic premises of the Rouse model are good. It may be necessary, however, to make minor modifications to the theory or improve the experimentation. It is noticeable that the friction factor in the theory has to be adjusted in an ad hoc way to comply with the molecular weight dependency of the viscosity. The mixing rule (eq. 4.1.2) for polymers should also be examined carefully. The ratio $(n_{33} - n_{22})$ to $(n_{11} - n_{22})$ would appear to be independent of any mixing rule or assumption about the friction factor, and this may be the strongest support for the molecular approach.

A good description of non-linear behaviour and molecular weight dependency of J_e is still problematic. However, the modifications proposed by Graessly (see Section 4.5) could be on the right lines. Two of the polystyrenes in this thesis fall within the scope of his second, more elaborate, theory for non-Newtonian flow¹⁷⁾. Styron 678 has M_w/M_n ratio of about two and S111 has M_w/M_n ratio of about one; for both eventualities tables are available of the viscosity and the reduced shear rate $\dot{\gamma}\tau$, where τ is the longest relaxation time of the Rouse theory¹⁷⁾. For Styron 678 at 190 °C, τ is about 0.25 s and for S111 about 0.5 s. The latter value is in good agreement with the longest relaxation time from stress-relaxation experiments on S111 at the same temperature¹⁸⁾. When these data are used, the viscosity curve (Fig. 5.34) for Styron 678 was in almost perfect agreement with Graessly's predicted curve - $\pm 5\%$. The fit for S111 was less good, but still acceptable. We use these results to show that present developments in the molecular theories, although in some aspects rather unsatisfactory, are very close to a correct description of experimentally found behaviour.

6.5 Steady Shearing - Oscillatory Shearing

The validity of the Cox-Merz relation was reconfirmed in all cases. The possibility of more general relations between quantities in steady shearing and oscillatory shearing have been examined. For this purpose, linear combinations $\eta'(\omega)$ and $\eta''(\omega)$ were used to reproduce the steady flow data. In this way, kernels could be generated to predict steady flow data from dynamic, linear viscoelastic, flow data. It was found that a single kernel could be used to describe the steady flow viscosity of several polystyrenes. However, the determined kernel may not have been unique as for each of the polystyrenes other combinations of η' and η'' gave an adequate description of the steady flow viscosity. The quoted combination was the only one which worked satisfactorily for all polystyrenes, the same relation did not work equally well for the polyethylenes.

For the application of the viscosity kernel to the normal stresses, the conclusion must be that this is generally not possible if accurate data are required.

The experimentally found kernels were not in good agreement with most of the theoretical proposals, which are to be found in the literature, as most of the latter show too sharp a decay.

Notwithstanding the problem of obtaining exact data, there is plenty of semi-quantitative agreement between the kernel method and the approach, whereby a sharp cut-off of the relaxation spectrum $N(\tau)$ is used. To illustrate this, let us evaluate to a first approximation the simple cut-off function, as defined by Booij¹⁹⁾ in the case of non-Newtonian viscosity.

We seek a solution for τ_m in the equality

$$\eta(q) = \int_0^{\tau_m} H(\tau) d\tau = \int_0^{\infty} H(\tau) K(q\tau) d\tau \quad (6.2)$$

For the present results we approximate the kernel $K(q\tau)$ to $[1 + c^2 q^2 \tau^2]^{-1}$.

This is equivalent to assuming that $\eta(q)$ and $\eta'(\omega)$ can be superimposed by horizontal shifts along the rate axis by a factor c^{-1} . As indicated earlier this is not a good description of the results, but it is far better than the assumption that $\eta(q)$ and $\eta'(\omega)$ superimpose directly and it gives the first approximation. The next step is to approximate $N(\tau)$ by the box function $\tau N(\tau) = H_0(\tau) = 1$, $0 < \tau < \tau_c$; $\tau N(\tau) = 0$, $\tau > \tau_c$. There is obtained for the physically realistic case $[\tau_m < \tau_c]$:

$$\tau_m = \frac{1}{qc} \tan^{-1}(qc\tau_c) \sim \frac{\pi}{2qc} \quad (6.3)$$

For this very simple model, the cut-off time of equation (6.2) is inversely proportional to q , a result born out by experience¹⁹⁾. From the present data